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CHEVRON CINCINNATI FACILITY

HOOVEN, OHIO

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1.0 INTRODUCTION

Chevron Environmental Management Company (Chevron) is performing final groundwater corrective measures implementation and monitoring of the remedy performance at the former Gulf Refinery located approximately 20 miles west of Cincinnati, Ohio, near the intersection of Ohio State Route 128 and US Highway 50, as shown on Figure 1-1. The groundwater remedy was designed to be protective of human health and the environment, with the long-term objective of reducing dissolved phase hydrocarbon concentrations to meet cleanup objectives. Achieving the long-term objective will take many years; therefore the following interim objectives have been adopted for the groundwater remedy:

- Monitor soil vapor concentrations and prevent migration of volatile petroleum hydrocarbons into indoor air above risk based limits
- Measure the stability of LNAPL and dissolved phase petroleum hydrocarbons
- Remove recoverable LNAPL to agreed upon end-points
- Stabilize the west bank of the Great Miami River to prevent erosion of soils containing petroleum hydrocarbons

Groundwater remediation and monitoring efforts are being conducted in accordance with a November 2006 Administrative Order on Consent (*2006 AOC*) between Chevron and the United States Environmental Protection Agency (USEPA; Docket No: RCRA-05-2007-0001). The primary components of the groundwater remedy specified in the *2006 AOC* include:

- Re-establishment of natural hydraulic conditions beneath the facility, Hooven, and off-site properties to the southwest (commonly referred to as the Southwest Quad) through discontinuance of year round groundwater recovery (although, as subsequently discussed, hydraulic containment via groundwater extraction from the production wells situated along the facilities eastern boundary were performed from March 2009 until March 2010)
- Focused LNAPL removal during periods of extreme low water table conditions through high-grade pumping over the next decade
- Combined operation of the horizontal soil vapor extraction (HSVE) system beneath Hooven with high-grade recovery (though the USEPA ordered discontinuance of the HSVE system between December 2007 and October 2009 while soil vapor monitoring was conducted by the USEPA Superfund Technical Assessment & Response Team)

- Continued seasonal operation of the Gulf Park biovent system during low water table conditions
- Engineered stabilization of the bank of the Great Miami River at the former refinery and Gulf Park to prevent erosion of soil containing petroleum hydrocarbons
- Long-term monitoring of natural source zone attenuation including dissolved and vapor phase biodegradation

A fundamental concept of the final groundwater remedy is the continued stability of the LNAPL and dissolved phase petroleum hydrocarbons. The majority of recoverable LNAPL has been removed beneath the former refinery and off-site properties over the past two decades. This is especially true in the upper and middle reaches of the smear zone, where LNAPL saturations are low. High-grade recovery is intended to focus on remaining LNAPL removal within the lower reaches of the smear zone and portions of the smear zone with the highest remaining LNAPL saturations. However, it is understood that the long-term remedy objective will be accomplished primarily through natural attenuation processes that drive contaminant degradation and removal over time.

A detailed discussion of the objectives and activities to be conducted to achieve the groundwater remedy goals, are described in the documents titled, *Remedy Implementation Plan (RIP) for Final Groundwater Remedy, Chevron Cincinnati Facility* (Trihydro 2007a) and the *Operation, Maintenance, and Monitoring (OMM) Plan for Final Groundwater Remedy, Chevron Cincinnati Facility* (Trihydro 2007b).

Some components of the *RIP* (Trihydro 2007a) and *OMM Plan* (Trihydro 2007b) were amended with a June 30, 2008 modification to the 2006 AOC, which was put in place per USEPA plans for conducting an independent vapor monitoring program in Hooven. The USEPA's Hooven vapor monitoring program was not completed by the end of 2008 as originally intended, so plans for monitoring and system operation during 2009 were further clarified in a February 18, 2009 letter from USEPA to Chevron. As such, the HSVE system remained inactive for 22 months between December 2007 and October 2009, including during the time of focused pumping of groundwater and removal of LNAPL (high-grade pumping) beginning in August 2009, when it normally would have been operated in accordance with the 2006 AOC. As a result, the soil vapor concentrations measured between August and October 2009, during high-grade operation, represent an engineered worst case condition that has not been observed previously under natural conditions. The results of the additional soil vapor monitoring performed by Chevron when the HSVE system was inactive are discussed in Section 3.0 herein and additional information is included within the *Hooven Vapor Site Conceptual Model Update, Chevron Cincinnati Facility, Hooven, Ohio (Hooven Vapor SCM Update, Trihydro 2010)*.

1.1 SUMMARY OF SITE CONCEPTUAL MODEL

A detailed site conceptual model (SCM) for groundwater was presented in the *First 2008 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2009a). A summary of the SCM is provided herein including updates made using data collected during assessment and routine monitoring performed during 2009.

Figure 1-2 shows a diagrammatic SCM for the facility, Hooven, and Southwest Quad.

1.1.1 SETTING

Refinery operations at the former Gulf Oil refinery began in 1931. Chevron acquired Gulf Oil Company in 1985 and that same year, an oily sheen was observed on the Great Miami River along the southeast portion of the facility. Hydraulic containment measures were implemented to minimize migration of petroleum hydrocarbons off-site. The refinery ceased production in 1986 and the refinery infrastructure was subsequently dismantled. Interim measures performed at the facility since early 1985 focused on hydraulic control of LNAPL and dissolved phase petroleum hydrocarbons by extracting groundwater and creating inward hydraulic gradients. These measures were expanded to include excavation of refinery related wastes; soil vapor extraction and six-phase heating beneath the Islands; bioventing beneath Gulf Park; and operation of the HSVE system designed to remove hydrocarbons beneath State Route 128 and Hooven. Historic remediation activities have recovered millions of gallons of LNAPL.

The former refinery is situated in a glacial valley incised into Ordovician-age shale and partially filled with glacial outwash and fluvial deposits of the Great Miami River (Spieker and Durrell 1961, Spieker 1968, Watkins and Spieker 1971). The fluvio-glacial aquifer ranges from approximately 20 to 100 feet thick, and is composed of dominantly coarse sediment, referred to as the Buried Valley Aquifer. An upward fining sequence is present in areas along the riverbank and flood plain on the former refinery. In addition, a clayey-silt layer is exposed at the ground surface in the western portion of Hooven with a thickness of at least 10 feet along the western edge of town. This layer serves as an apparent aquiclude with runoff flowing eastward over the shallow aquiclude before descending towards the groundwater table and joining regional flow.

Groundwater within the Buried Valley Aquifer generally flows from north to south, although episodic flooding tends to result in redirection of the flow to the west for periods ranging from days to weeks dependant on the magnitude of the flood event. A partially penetrating sheet pile wall was installed at the facility as part of the riverbank stabilization measures between September and December 2008. The partial penetrating wall does not affect horizontal flow conditions (i.e. flow direction primarily parallel to the river bank) within the Buried Valley Aquifer under ambient

conditions. However, as designed, communication between groundwater and surface water has been dampened locally near the barrier wall during periods of increasing or decreasing discharge within the Great Miami River.

1.1.2 SOURCE

Refinery operations terminated in 1986, and the distribution of LNAPL stabilized as gravity and capillary forces approached equilibrium. Vertical smearing of the LNAPL occurred over time as a result of seasonal fluctuation of the water table, leaving some LNAPL within the pore spaces below and above the water table. The top and bottom of the “smear zone” are roughly coincident with the historic high and low groundwater elevation. Therefore, some smear zone is exposed above the water table, even during periods of seasonal high groundwater, although the maximum exposure of LNAPL occurs during low water table events. The thickness of the smear zone generally increases from inches at the plume periphery, to as much as 20 feet in locations of the production wells. The depth to the top of the smear zone varies across the site, from as little as 10 feet near the Great Miami River, to approximately 30 feet across most of the former process areas and tank farms, 40 feet beneath the Southwest Quad, and up to 60 feet under the town of Hooven.

Petroleum hydrocarbon liquids are a mixture of hundreds of individual compounds from many families, including aliphatics, aromatics, paraffins, isoparaffins, olefins, and naphthalenes. Each compound has somewhat different physical, chemical, and toxicological properties, but some are sufficiently volatile and toxic to pose a potential human health risk via dermal contact, ingestion, and inhalation if present at sufficient concentration. In the area adjacent to the distribution of LNAPL, some hydrocarbons dissolve in groundwater and migrate as solutes in the aqueous phase. Volatilization from LNAPL or dissolved phase hydrocarbons can produce vapors in the unsaturated zone immediately above the water table.

1.1.3 PLUME STABILITY

A fundamental concept of the final groundwater remedy is the continued stability of LNAPL and dissolved phase petroleum hydrocarbons. The majority of recoverable LNAPL has been removed from beneath the former refinery and off-site properties over the past two decades. This is especially true in the upper and middle reaches of the smear zone, where LNAPL saturations are low. High-grade recovery is intended to focus on removal of LNAPL within the lower reaches of the smear zone and portions of the plume with the highest remaining LNAPL saturations. However, it is understood that the long-term remedy objective will be accomplished primarily through natural processes that drive contaminant degradation and removal over time.

The LNAPL and dissolved phase plume boundaries are generally coincident at the up-gradient and lateral edges of the smear zone (i.e., western limit in Hooven and eastern limit along the Great Miami River), where dissolved phase petroleum hydrocarbons are generally indicative of LNAPL within the smear zone. Whereas, in the primary flow direction towards the south, a dissolved phase “halo” extends several hundred feet down-gradient from the LNAPL plume boundary.

Dissolved phase plume stability is expected to continue over the long-term, however, it was anticipated that some re-distribution of dissolved phase hydrocarbons would occur at the down-gradient edge of the plume after discontinuance of hydraulic containment that was performed for more than two decades. It is anticipated that the dissolved phase plume stability will become re-established during the first few years after pumping is discontinued. It should be noted that detections of dissolved phase benzene in monitoring wells MW-35 and MW-133 were observed during monitoring in 2009, as discussed further in Section 2.2. These detections of benzene in groundwater are not believed to be associated with re-distribution of the dissolved phase limits. The benzene detected in these two wells is likely derived from an alternate source in the Southwest Quad, as the measured dissolved phase concentrations do not follow trends that would be expected if contaminants were migrating down-gradient from the smear zone limits to the point of compliance (POC) well.

The primary driver for plume stability is believed to be active biodegradation along the boundaries of the smear zone (i.e., up- and down-gradient limits of the smear zone, lower reaches of the smear zone within the saturated zone, and upper contact of the smear zone in the unsaturated zone). Most petroleum hydrocarbons are readily degradable by soil microorganisms in the presence of oxygen (O_2), a process referred to as aerobic biodegradation. Petroleum hydrocarbons are also degraded by soil microorganisms in the absence of O_2 via anaerobic respiration, but generally at a slower rate compared with aerobic degradation.

The pathway for migration of petroleum hydrocarbon in soil vapor into structures located in Hooven and the Southwest Quad is considered incomplete. Soils within the vadose zone to the west of the refinery are predominantly sand and gravel, which allow water to drain relatively freely; therefore, the pore-spaces are mostly air-filled, which provides a pathway for vapor migration. The migration of hydrocarbon vapors from the vapor source at depth is retarded by biological degradation where soil microbes metabolize hydrocarbon vapors as a source of energy. Beneath Hooven, where the vadose zone is nearly 60 feet thick, the hydrocarbon vapors are generally reduced through aerobic biodegradation where O_2 in the atmosphere diffuses down into the unsaturated zone and is reduced along with the petroleum hydrocarbon vapors. As discussed in Section 1.1.5, alternate sources are present in the vadose zone from

surface releases of petroleum and non-petroleum related chemicals in Hooven. These releases affect the vertical profile of constituents of concern and fixed gases through utilization of O_2 and mixing of vapors within the intermediate portions of the vadose zone.

Microbiological degradation can also occur in the absence of O_2 within the vadose zone, where secondary oxidizers such as iron, sulfate, nitrates, etc. are reduced producing methane (CH_4). The CH_4 will subsequently diffuse upward and is generally degraded at shallower intervals where O_2 concentrations are sufficient. Anaerobic degradation is typically observed in the deeper intervals above the LNAPL and dissolved phase plume; however anaerobic conditions can persist in the intermediate portions of the vadose zone during seasonally low water table conditions if secondary sources of petroleum hydrocarbons are present in the shallow subsurface utilizing available O_2 .

Biodegradation is a primary driver not only for stability of the vapor and dissolved phase petroleum hydrocarbons, but also for hydrocarbon mass reduction throughout the plume. Aerobic and anaerobic processes reduce contaminant mass in the dissolved and vapor phase. Whenever O_2 is available, aerobic biodegradation processes predominate. Aerobic degradation processes are the dominant mechanism for reductions in petroleum hydrocarbon concentrations in the plume periphery. Within the interior portions of the plume where O_2 is depleted, anaerobic biodegradation processes will tend to dominate. These anaerobic processes are expected to continue in portions of the smear zone where secondary oxidizers are available, given the relatively consistent supply of petroleum hydrocarbons (i.e., source of carbon) from the smear zone.

1.1.4 RECEPTOR

Receptors that have the potential to be affected by LNAPL and dissolved phase petroleum hydrocarbons include residents within Hooven, commercial workers in business situated in the Southwest Quad, sensitive ecological communities along the Great Miami River, visitors and workers employed in remedy support and redevelopment activities on the former refinery, and trespassers coming onto the facility property. As the groundwater beneath the facility, Hooven, or Southwest Quad is not used for drinking purposes or secondary uses (e.g., irrigation, bathing, etc.) ingestion and dermal contact with dissolved phase petroleum hydrocarbons associated with the former refinery will not occur. Administrative and engineering controls, as well as personal protective equipment will be used as appropriate to prevent site workers and visitors from unacceptable levels of exposure to LNAPL or dissolved phase petroleum hydrocarbons during redevelopment on the former refinery. Bank stabilization measures along the Great Miami River prevent soil containing petroleum hydrocarbons from eroding into the river or the discharge of dissolved phase petroleum hydrocarbons to surface water.

With respect to vapor intrusion, the receptor would be any occupant of a building on the former refinery, in Hooven, or to the southwest if subsurface vapors entered that building at concentrations that pose a potential health risk. If soil vapors diffuse within the “zone of influence” of a structure without degrading, they will become available to be transported into the structure via advection and convection through drains, cracks, utility entrances, sumps, or other permeable discontinuities in the building floor or basement walls. Wind load on the side of a building, barometric pressure changes, HVAC system operation, or temperature differences can all contribute to building depressurization that can drive advection. Most of these processes are reversible, so gases generally flow into and out of buildings under varying conditions. Atmospheric air also enters buildings through doors, windows, and small openings, and the rate of air exchange in buildings typically reduces soil vapor concentrations by a factor of 100 to 10,000 (Johnson 1999), depending on building design, construction, use, maintenance, soil conditions, weather conditions and similar factors.

The vapor intrusion pathway in Hooven was demonstrated to be incomplete during the subsurface investigation completed in 2005, through characterization of the contaminant source, soil vapor, and migration pathway. In addition, the soil vapor data collected from the nested monitoring wells from 1997 to 1999 and following the 2005 investigation have also indicated vapors from the plume are not migrating from the smear zone to indoor air within the residences, businesses, or school at concentrations sufficient to pose an unacceptable excess health risk. In portions of the Southwest Quad overlying the smear zone, commercial structures were constructed with a passive vapor barrier beneath the slab as a protective measure for inhibiting migration of vapors into the building, if present.

1.1.5 ALTERNATE SOURCES

There are several potential alternate sources of LNAPL and dissolved phase petroleum hydrocarbons within proximity of the former refinery. These include a former service station (currently a non-commercial automotive service center) located directly north of the facility, former operations at the Dravo quarry including several diesel and gasoline underground storage tanks removed in 1991, the Kroger gasoline and diesel service station, underground storage tanks removed at the Hooven Elementary School, underground storage tanks located at the Hooven Fire Station, dry wells installed in the Southwest Quad, the Whitewater Reclamation (formerly Golsch) construction and demolition landfill, surface releases associated with vehicles travelling on Ohio State Route 128 and United States Highway 50, surface releases from vehicles located in parking lots across the Southwest Quad, commercial businesses (e.g., automotive repair, long-haul trucking, and construction lay down yards) located within Hooven and the Southwest Quad, as well as local point sources associated with residential, municipal and commercial activities in the Southwest Quad and Hooven. In addition, each of the residences and other occupied structures in Hooven maintained an individual septic system to treat wastewater, prior to extension of a municipal sanitary sewer system into the community in 2006.

Several studies including DeWalle et. al. 1985, Conn and Seigrist 2009 have documented releases of volatile petroleum related constituents from septic systems.

Volatile petroleum hydrocarbons are ubiquitous in indoor and outdoor air from industrial and commercial sources, automobiles, combustion sources (e.g., gasoline, fuel oil, natural gas, etc.), combustion byproducts (e.g., diesel, wood, coal, candles, etc.), water treatment chemicals and byproducts, a variety of different consumer products, small power tools, tobacco smoke, glues, household cleaners, carpeting, and furniture. Indoor air often contains measurable concentrations of volatile and semivolatile compounds from household activities, consumer products, building materials, furnishings, and outdoor air sources. Urban areas can also have shallow releases of hydrocarbons to the subsurface from sources similar to those described above. Therefore, hydrocarbon vapors are present in the vadose zone and indoor air in Hooven and the Southwest Quad associated with releases from these alternate surface sources.

1.2 PURPOSE

The primary purpose of this report is to provide a summary of the operations and monitoring conducted in accordance with the 2006 AOC, RIP (Trihydro 2007a), and OMM Plan (Trihydro 2007b) from July 1, 2009 to December 31, 2009. This report will also provide a summary of additional assessment and operational activities performed during the second half of 2009 including hydraulic control activities in the Southwest Quad, high-grade recovery activities, additional soil vapor monitoring performed in Hooven and the Southwest Quad, as well as installation of the hanging sheet-pile barrier in Gulf Park. The remainder of this report is organized into the following sections:

- Section 2.0 – Describes the infrastructure, methods, and results of monitoring activities conducted during the second semiannual monitoring period in 2009.
- Section 3.0 – Presents the preliminary qualitative and quantitative lines of evidence supporting the efficacy of natural attenuation mechanisms to degrade petroleum hydrocarbons within the smear zone.
- Section 4.0 – Provides the results of high-grade recovery operation completed between August and December 2009 including performance of the biologically enhanced granular active carbon (GAC) treatment and HSVE systems during this event.
- Section 5.0 – Describes the results of biovent system operation conducted in Gulf Park. This section also details the sheet pile barrier installation activities completed during the second half of 2009 along the bank of the Great Miami River in Gulf Park.

2.0 MONITORING NETWORK AND RESULTS

The primary component of the final groundwater corrective measures program is routine monitoring to evaluate the progress towards meeting the interim and long term remedy objectives. The monitoring network has been established to meet multiple performance and compliance monitoring criteria including collection of data to support remedial system operation; confirmation of high-grade pumping and HSVE system effectiveness; determination of compliance at boundaries where sensitive receptors are present; and evaluation of natural attenuation mechanisms. For the purpose of this report, monitoring has been divided into the following activities:

- Fluid level gauging including continuous monitoring using pressure transducers as well as weekly, monthly, and bimonthly manual measurements
- Groundwater sampling to demonstrate dissolved phase plume stability, protection of sensitive receptors, and efficacy of monitored natural attenuation
- Lysimeter monitoring to collect data regarding precipitation infiltrate to assist in understanding electron acceptor flux into the upper plane of the smear zone
- ROST monitoring to confirm stability of the LNAPL plume at the lateral edge of the smear zone
- River monitoring to evaluate groundwater and surface water quality adjacent to, beneath, and within the Great Miami River
- Vapor monitoring to track the vapor intrusion pathway beneath Hooven and the Southwest Quad and evaluate natural attenuation mechanisms in the vadose zone

The following sections describe the results of monitoring conducted to support the groundwater remedy between July 1 and December 31, 2009. A description of the methods used for installation, monitoring, and analysis have been previously described within the *RIP* (Trihydro 2007a) and *OMM Plan* (Trihydro 2007b). Additional information pertinent to these activities is described herein when deviations from these plans was necessary.

2.1 FLUID LEVEL MONITORING

Pressure transducers are generally deployed across the monitoring well network listed on Figure 2-1 to evaluate rapid fluctuations in hydraulic conditions across the facility. The pressure transducers are relocated as the goals of short term monitoring change such as during flood events or groundwater recovery. Transducers log groundwater elevations on a

daily basis. High frequency groundwater elevation data recorded using the pressure transducers are provided in Appendix A.

Pressure transducers were relocated in March 2009 as hydraulic control of groundwater was re-established down-gradient of the facility using production wells PROD_15 and PROD_24 and then again on August 19, 2009 before the start of high-grade pumping. Pressure transducers were deployed in an expanded network (including wells MW-4, MW-10, MW-17, MW-18R, MW-19, MW-20S, MW-21, MW-26R, MW-35, MW-44S, MW-81S, MW-85S, MW-93S, MW-94S, MW-96S, MW-99S, MW-101, MW-112, MW-131, PROD_15, PROD_19, PROD_20, PROD_24 and RBGP-44) across the site, Hooven, and Southwest Quad to allow continuous monitoring of hydraulic gradients during high-grade recovery. Section 2.2 provides a further explanation of the groundwater monitoring results and re-initiation of hydraulic controls at the down-gradient limits of the facility.

Manual fluid level gauging is conducted on a bimonthly basis in each of the monitoring wells located on the facility, Hooven, Southwest Quad, and Gulf Park. In addition, fluid levels are gauged weekly in select groundwater monitoring wells, and river bank gauging point RBGP-44 located along the west bank of the river. Weekly gauging in these wells is conducted to supplement the bimonthly fluid level measurements in tracking trends in river and groundwater table elevations, as wells as LNAPL thickness. The number of wells included in the weekly fluid level monitoring was increased both onsite and in the Southwest Quad following the resumption of hydraulic control using production wells PROD_15 and PROD_24 in accordance with the submitted *Work Plan for Contingency Measures in the Southwest Quad* (Trihydro 2009d). Between July 1 and August 14, 2009 fluid levels were gauged on a weekly basis in selected monitoring wells (including wells RBGP-44, GPW-5S, MW-1R, MW-12, MW-20S, MW-26R, MW-35, MW-37, MW-81S, MW-93S, MW-94S, MW-96S, MW-100S, MW-101, MW-112, MW-115S, MW-120, MW-128, MW-131, MW-132, MW-133, MW-134, MW-138, MW-139, MW-140, MW-141, MW-142, PROD_15, PROD_24, and TH-2).

The list of monitoring wells that were gauged on a weekly basis was subsequently modified during high-grade pumping performed between August 19 and December 14, 2009, as outlined in the *OMM Plan* (Trihydro 2007b) and *First 2008 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2009a). Fluid levels were manually gauged from the following wells on a weekly basis during high-grade recovery: wells RBGP-44, GPW-5S, L-7, MW-1R, MW-4, MW-10, MW-17, MW-18R, MW-20S, MW-20D, MW-21, MW-26R, MW-35, MW-37, MW-44S, MW-48S, MW-58S, MW-62, MW-81S, MW-85S, MW-88, MW-92S, MW-93S, MW-94S, MW-95S, MW-96S, MW-99S, MW-100S, MW-101, MW-112, MW-115S, MW-120, MW-121, MW-122, MW-124, MW-125, MW-126, MW-128, MW-129, MW-131, MW-132, MW-133, MW-134, MW-138, MW-139, MW-140, MW-141, MW-142,

PROD_12, PROD_15, PROD_19, PROD_20, PROD_24, and TH-2. At the conclusion of high-grade recovery, weekly monitoring reverted back to those wells monitored in support of evaluating hydraulic control using production wells PROD_15 and PROD_24.

Appendix B provides manual fluid level gauging data collected during the second half of 2009. Potentiometric surface maps for July, September, and November 2009 generated using data collected during bimonthly monitoring are provided as Figures 2-2 through 2-4. Groundwater flow in the Buried Valley Aquifer is generally to the south under non-stressed (i.e., non-pumping) conditions. The potentiometric surface map generated using fluid level data collected on July 29, 2009 shows that groundwater flow was predominantly towards the depressions created through groundwater recovery using production wells PROD_15 and PROD_24 in the southern portions of the facility and Southwest Quad. Groundwater flow during high-grade pumping, as depicted on Figures 2-3 and 2-4, show a larger radius of influence and increased groundwater depression while pumping from production well PROD_20 on September 30, 2009, and from wells PROD_19 and PROD_20 on November 30, 2009.

2.2 DISSOLVED PHASE MONITORING

Dissolved phase monitoring is conducted at the facility, Hooven, and Southwest Quad to assess plume stability, evaluate natural attenuation within the saturated portions of the smear zone, and measure performance of the final groundwater remedy. Groundwater samples are analyzed for the constituents of concern including benzene, ethylbenzene, toluene, total xylenes, chlorobenzene, arsenic, and lead. Benzene is the constituent most frequently reported in groundwater samples above remedial objectives, with historic concentrations as high as 13 milligrams per liter (mg/L). Dissolved phase benzene is not generally detected more than a few hundred feet outside the LNAPL smear zone, due to intrinsic biodegradation at the plume periphery.

Groundwater samples are also collected from selected wells for analysis of natural attenuation indicators including alkalinity, total calcium, total chloride, chemical oxygen demand, ferric iron (Fe^{3+}), ferrous iron (Fe^{2+}), total iron, dissolved manganese, total manganese, CH_4 , nitrogen, nitrogen as ammonia, nitrate, nitrite, total potassium, total sodium, sulfate, sulfide, and total organic carbon.

Field forms for groundwater samples collected between July and December 2009 are included in Appendix C. Laboratory analytical reports for groundwater samples collected during the second 2009 semiannual monitoring period are provided in Appendix D-1. Data validation reports for each of the analytical packages provided by the laboratory

are provided in Appendix D-2. The following subsections present the results of dissolved phase monitoring conducted between July and December 2009.

2.2.1 SENTINEL AND POINT OF COMPLIANCE MONITORING

There are three sentinel wells (MW-35, MW-131, and MW-132) and four POC monitoring wells (MW-37, MW-120, MW-133, and MW-134) located at the down-gradient edge of the dissolved phase plume in the Southwest Quad. The sentinel and POC monitoring networks are presented on Figure 2-5. Groundwater samples were collected from the sentinel and point of compliance monitoring wells during September and October 2009, as part of semiannual monitoring activities in accordance with the schedule describe in the *OMM Plan* (Trihydro 2007b).

Groundwater analytical results for the dissolved phase constituents of concern are provided on Table 2-1. Dissolved arsenic was detected in samples collected from sentinel well MW-131 in July 2009 and from POC well MW-37 in October 2009 at estimated concentrations of 0.001 and 0.003 mg/L, respectively. As reported in the *Evaluation of Background Metal Concentrations in Ohio Soils* (Cox-Colvin & Associates, Inc. 1996) and the *Closure Plan Review Guidance for RCRA Facilities* (OEPA 1999), several metals including arsenic and lead are naturally occurring in soils across Ohio and the United States. Arsenic and lead have been sporadically detected in groundwater collected from monitoring wells located throughout the Southwest Quad over the more than two decades of monitoring.

In addition, dissolved phase benzene was reported in the groundwater sample collected from POC monitoring well MW-133 during quarterly monitoring in July 2009 at a concentration of 0.051 mg/L. Dissolved phase benzene was first detected in this well during monitoring performed in February 2009. In response, additional monitoring was performed within selected sentinel and point of compliance wells in the Southwest Quad, hydraulic controls were resumed using production wells PORD_15 and PROD_24, five monitoring wells were installed up-gradient of sentinel well MW-35, and a work plan for contingency measures was prepared. A discussion of these activities conducted in response to the dissolved phase benzene measured in the sentinel and point of compliance wells is provided in the following subsection.

2.2.1.1 RESPONSE TO DISSOLVED PHASE BENZENE DETECTIONS

Hydraulic control of groundwater in the Southwest Quad was re-initiated via pumping from production wells PROD_15 and PROD_24. These two production wells were restarted on March 29, 2009 with groundwater primarily extracted from production well PROD_15 at a rate of 875 to 1,000 gallons per minute (gpm) and secondarily from well

PROD_24 at a rate between 250 and 450 gpm from March 29 to August 10, 2009, with the flow rate subsequently increased to 750 gpm. Hydraulic containment using these two wells ceased during seasonal high-grade pumping which was performed between August 19 and December 14, 2009. High-grade pumping was discontinued due to ambient rebound of the water table above trigger levels in wells MW-20S, MW-93S, MW-96S, and MW-99S. On December 15, 2009, hydraulic control was reinitiated beneath the Southwest Quad using production well PROD_15 (operated at 1,000 gpm) combined with PROD_24 (average pumping rate of 400 gpm) from December 15, 2009 to February 25, 2010, and then PROD_23 (average pumping rate of 400 gpm) from February 25 to March 9, 2010. The USEPA approved discontinuance of hydraulic containment beneath the Southwest Quad and return to ambient groundwater conditions on March 8, 2010. The results of the high-grade pumping event completed in 2009 are provided in Section 4.0.

As reported in the *First 2009 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2009e), five additional groundwater monitoring wells (MW-138 through MW-142) were installed in March 2009 up-gradient of sentinel well MW-35 to characterize the relationship between the dissolved phase detections reported in this monitoring well, POC well MW-133, and those detected in the up-gradient portions of the smear zone in the Southwest Quad. The frequency of fluid level and dissolved phase monitoring was increased in the Southwest Quad in response to the benzene detected in groundwater samples collected from POC well MW-133. As discussed in Section 2.1, fluid levels have been manually gauged on a weekly basis and pressure transducers have been deployed in an expanded network within the Southwest Quad to allow continuous monitoring of hydraulic gradients and LNAPL thicknesses. In addition, groundwater samples were collected and analyzed for the constituents of concern on a monthly basis from wells MW-35, MW-133, and newly installed wells MW-138, MW-139, and MW-142 since the first semiannual monitoring event. Finally, groundwater samples were collected from monitoring well MW-141 as part of the quarterly monitoring activities. Groundwater samples could not be collected from monitoring well MW-140, located within the smear zone, during the second half of 2009 due to the continued presence of LNAPL within the well.

Groundwater samples were analyzed for the dissolved phase constituents of concern. Groundwater analytical results since November 2008 are summarized on Table 2-1 and Figure 2-6. Dissolved phase petroleum hydrocarbons were irregularly detected in the sentinel and POC monitoring wells prior to restarting the production wells in late March, with detections only in samples collected from wells MW-35 and MW-133.

Dissolved phase benzene concentrations decreased rapidly in sentinel well MW-35 following resumption of hydraulic controls to the point where benzene was no longer measured above detection limits in samples collected after early

April 2009. Whereas, concentrations of dissolved phase benzene persisted in POC monitoring well MW-133 until September 2009, despite re-establishment of hydraulic controls.

As depicted on Figure 2-6, well MW-139 is the nearest up-gradient well where benzene has been reported in samples collected since May 2009. Monitoring well MW-139 is located more than 400 feet up-gradient of POC well MW-133 and is situated at the lateral limit of the smear zone. If the smear zone was the source of the dissolved phase benzene it would be expected that the constituent concentrations would show a consistent decreasing trend in the down-gradient direction. Constituent concentrations have not behaved in this manner in the Southwest Quad, with dissolved phase benzene decreasing to non-detect concentrations down-gradient of the smear zone and then increasing again at the POC boundary well MW-133. Potentiometric surface maps generated using data prior to reinitiating hydraulic controls do not indicate preferential flow paths beneath the Southwest Quad. If there was redistribution of dissolved phase impacts it would be expected to occur across the entire smear zone and the constituents would be more uniformly detected across the down-gradient monitoring network. This is suggestive of a localized alternate source of benzene.

On October 1, 2009 Chevron submitted the *Work Plan for Contingency Measures in the Southwest Quad, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2009d). The work plan was approved on March 4, 2010 pending modifications. Chevron submitted the modified work plan on April 1, 2010. This work plan describes the nature of the dissolved phase constituents measured in the Southwest Quad and the lines of evidence supporting an alternate source for benzene measured in samples collected from sentinel well MW-35 and POC well MW-133. In accordance with this work plan, groundwater will be monitored monthly in wells within and down-gradient from the smear zone to closely track the dissolved phase constituent distribution as ambient groundwater conditions become re-established. If the results confirm that constituents from the plume are not migrating to the POC, then long-term operations and monitoring will revert to the protocols outlined in the *OMM Plan* (Trihydro 2007b).

If future monitoring results indicate that (1) dissolved phase constituents of concern are present in monitoring wells from the smear zone in a continuous trend down-gradient to the POC boundary, (2) concentrations of dissolved phase constituents measured in the sentinel and point of compliance wells are in good agreement with the expected concentrations based on the effective solubility of constituents present within the smear zone, and (3) the concentration of a dissolved phase constituent of concern listed on Table 1 of the 2006 AOC exceeds the USEPA Maximum Contaminant Level (MCL, USEPA 2009), contingency measures will be implemented.

2.2.2 PERIMETER, INTERIOR, AND SUPPLEMENTAL MONITORING

As discussed in the SCM presented in Section 1.0 and supported by data collected to date, the LNAPL and dissolve-phase petroleum hydrocarbons are laterally stable and degrading over time. Remaining LNAPL in the smear zone is gradually depleted through several mass loss mechanisms including dissolution into groundwater and subsequent dispersion and biodegradation, as well as volatilization and degradation within the vadose zone. As such, groundwater samples were collected from three groups of monitoring wells for evaluation of natural attenuation mechanisms within the saturated zone: perimeter, interior plume, and supplemental monitoring wells.

- Perimeter groundwater monitoring wells include those wells situated at the margins of the smear zone but not considered to be compliance boundaries for dissolved phase petroleum hydrocarbons in the saturated zone. Monitoring wells that are included in this network include MW-26R, MW-33, MW-48S, MW-85S, MW-94S, MW-95S, MW-100S, MW-104S, and MW-115S. A groundwater sample could not be collected from monitoring wells MW-85S and MW-94S during the second 2009 semiannual monitoring period due to the presence of LNAPL within the well.
- Interior plume monitoring wells are those wells located within the smear zone that will be tracked on a consistent basis over the course of the remedy and include eleven wells: MW-10, MW-17, MW-18R, MW-20S, MW-22, MW-58S, MW-81S, MW-85D, MW-88, MW-93S, and MW-96S. A groundwater sample could not be collected from monitoring wells MW-18R, MW-20S, MW-58S, MW-81S, MW-88 and MW-96S, during the second 2009 semiannual monitoring period due to the presence of LNAPL within these wells.
- Supplemental monitoring wells include additional wells that will be targeted for sampling to support evaluation of natural attenuation over the long-term remedy. The supplemental well network may be modified based upon data gaps identified during previous monitoring periods. Supplemental monitoring wells sampled during the second semiannual monitoring period in 2009 include wells L-1RR, MW-21, MW-51, MW-64, and MW-80.

Groundwater analytical results for the dissolved phase constituents of concern reported in samples collected from the perimeter, interior plume, and supplemental monitoring wells are provided on Table 2-2.

Groundwater samples were also collected from 12 monitoring wells for analysis of natural attenuation indicators during the second semiannual monitoring period including wells L-1RR, MW-21, MW-33, MW-35, MW-37, MW-38, MW-51, MW-52, MW-93S, MW-100S, MW-112, MW-114, MW-115S, MW-131, and MW-133. Groundwater analytical results for the dissolved phase natural attenuation indicators are included on Table 2-3. Interpretation of the dissolved phase analytical results is provided in Section 3.0.

2.3 LYSIMETERS

Between September 22 and September 30, 2008, two soil moisture lysimeters were constructed at the grouped media locations near wells MW-18, MW-20, MW-21, and MW-93, in accordance with details presented in the *RIP* (Trihydro 2007a). The lysimeters are used to measure the makeup of recharge water (particularly oxidizers) from infiltrating precipitation and evaluate the contribution of the makeup water to biodegradation within the upper limits of the saturated zone. A shallow and deep lysimeter were installed at each grouped media location, the first set at a depth well above the smear zone and the second set at an elevation within or near the upper smear zone limit. Placement of each lysimeter was a function of the elevation of the top of the smear zone.

Each lysimeter consists of a small ceramic receptacle (4-inch diameter by 18-inches tall) placed into a borehole to the target depth. The ceramic receptacle has two Teflon tubes extending to the ground surface, a pressure-vacuum access tube and a sample discharge tube. A vacuum is applied to the lysimeter ceramic cup which wicks precipitation infiltrate from the vadose zone and can subsequently be extracted by applying pressure to the receptacle.

In accordance with the *OMM Plan* (Trihydro 2007b) a vacuum was applied to the shallow and deep lysimeters on December 2, 2009. Subsequently, on December 9, the rainwater infiltrate was collected from the shallow lysimeters. Samples were not collected from the deep lysimeter at each location due to sufficient recovery in the shallow lysimeter. Infiltrating precipitation collected from the lysimeters was analyzed for dissolved O_2 and oxidation-reduction potential (ORP) in the field prior to preserving the samples and submitting them for laboratory analysis of nitrate, sulfate, dissolved/total iron, dissolved/total manganese, and CH_4 .

Field forms for samples collected from the lysimeters in December 2009 are included in Appendix C. Laboratory analytical reports for the lysimeter samples are provided in Appendix D-1 and data validation reports for each of the analytical packages provided by the laboratory are included in Appendix D-2. The lysimeter sampling results are presented in Table 2-4.

Lysimeter sampling results indicate that the chemistry of precipitation infiltrate varies across the smear zone. The concentrations of dissolved O_2 measured in the infiltrate collected from lysimeter L-21S (northernmost location) and lysimeter L-18S (located over the core portion of the smear zone) were generally elevated (5.0 and 2.8 mg/L, respectively) while other electron acceptors (sulfate and nitrate) were relatively low. Reduced byproducts including dissolved manganese and CH_4 were elevated within the samples collected from these locations. This may be an

indication of ongoing attenuation of petroleum hydrocarbons, and subsequent partitioning of CH₄ and volatile petroleum hydrocarbons from soil vapor to pore water within the vadose zone.

In the southern portions of the smear zone (lysimeters L-20S and L-93S), the pore water contains high levels of dissolved O₂, sulfate, and nitrate, which act as electron acceptors for biodegradation. Reduced by-products including dissolved iron, dissolved manganese, and CH₄ were all reported at low concentrations or non-detect in the infiltrate samples collected from these two lysimeters.

Precipitation and subsequent infiltration comprise an important component of the aquifer water budget. Much of this infiltrating water contains electron acceptors that are used by microorganisms in the smear zone to destroy hydrocarbons. The lysimeter data are useful in understanding this process. This is demonstrated by the assimilative capacity bar graph presented in Figure 2-7. The assimilative capacity is estimated by summing the concentrations of electron acceptors and subtracting biodegradation byproducts, scaled to stoichiometric coefficients for biodegradation of hydrocarbons. As shown on this figure, pore water in the northern and central portion of the smear zone (as evaluated using lysimeters L-21S and L-18S) has a relatively low assimilative capacity. This is an indication that precipitation infiltrate at these locations does not have significant potential to further degrade hydrocarbons. On the other hand, the assimilative capacity of infiltrate in the southern portions of the smear zone (assessed using lysimeters L-20S and L-93S) is much higher.

2.4 ROST MONITORING

Three ROST monitoring transects (RT-1 through RT-3) are in place perpendicular to the leading edge of the LNAPL plume, as shown in Figure 2-5. ROST technology was identified as the preferred tool for monitoring the potential for LNAPL migration at the leading edge of the plume because it is designed to provide real-time analysis of the physical and chemical characteristics of the distribution of petroleum hydrocarbons to distinguish between soils containing LNAPL and those outside of the smear zone.

The ROST monitoring transects consist of blank polyvinyl chloride (PVC) casing above the smear at three locations within each transect: an interior location (I) situated at the approximate lateral limit of the smear zone, an intermediate location (M) located 20-feet from the approximate lateral limit of the smear zone, and an outer location (O) installed 40-feet from the approximate lateral limit of the smear zone. ROST technology and installation methodology is presented in greater detail in the *RIP* (Trihydro 2007a).

Monitoring within the ROST monitoring wells was conducted between December 16 and 18, 2009. The tool was advanced from approximately 5 feet above the water table to approximately 5 feet below the water table in each of the wells. ROST monitoring results are provided in Appendix E. Data collected during the first half of 2009 indicate that the smear zone is stable. There was not an indication of the presence of LNAPL within any of the intermediate or outer ROST monitoring wells based on laser induced fluorescence measurements in the three transects.

2.5 RIVER MONITORING

A partially penetrating sheet pile barrier wall and bank stabilization measures were installed along the west bank of the Great Miami River between September and December 2008. As part of these bank stabilization measures, a barrier wall performance monitoring network was installed along the restored river bank in accordance with the *Performance Monitoring Plan, Sheet Pile Barrier Along Great Miami River, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2007c). This work plan specified measures to characterize baseline conditions and monitor performance of the partially penetrating sheet pile wall during implementation of the final corrective measures for groundwater. The performance of the sheet pile wall is monitored by observing the hydraulic gradients in groundwater and surface water, as well as evaluating groundwater, hyporheic water, and surface water quality over time.

The barrier monitoring network is comprised of three monitoring transects along the northern, central, and southern portions of the barrier wall as illustrated on Figure 2-8. Each transect includes a groundwater monitoring nest (shallow, intermediate, and deep wells) situated inboard of the sheet pile wall and a groundwater monitoring nest located on the outboard side of the wall. In addition, a hyporheic/surface water monitoring well was also constructed outboard of the wall at each monitoring transect. A description of the installation and construction details for the sheet pile wall, stabilization measures, and performance monitoring network is provided in the *Second 2008 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2009b).

2.5.1 FLUID LEVEL MONITORING

Pressure transducers were deployed on April 27, 2009 in the groundwater and surface water monitoring wells in the northern and southern monitoring transects to evaluate horizontal and vertical gradients across the partial penetrating barrier wall. Transducers are programmed to record groundwater and surface water elevations on an hourly basis. High frequency groundwater elevation data recorded using the pressure transducers are provided in Appendix A. Manual fluid level gauging was also conducted on October 2 and December 1, 2009 to supplement the transducer data and measure LNAPL gradients (if present) within the inboard portions of the barrier wall. LNAPL was not detected in

any of the monitoring wells situated on the west bank of the river between July and December 2009. Manual fluid level measurements are included in Appendix B.

Transducer data from select monitoring wells was used to illustrate vertical hydraulic gradients on the interior and exterior of the barrier wall at the north and south monitoring transects (Figure 2-9 and Figure 2-10). Along the northern transect (shown on Figure 2-9), the groundwater elevation on the interior of the wall was generally lower than the surface water elevation. In addition there is a consistent downward gradient on the outboard side of the wall with a corresponding upward gradient on the interior portion of the wall. This indicates that there may be some component of surface water recharge to the Buried Valley Aquifer, although this component of flow is small as the principal groundwater flow direction is parallel to the riverbank.

At the southern transect (shown on Figure 2-10), groundwater elevations and surface water elevations fluctuate, with periods of time where surface water is higher than groundwater and periods where groundwater is higher than surface water. There is a downward gradient primarily observed on the outboard side of the partially penetrating sheet pile wall that reverses when river stage increases. On the interior portions of the wall there was essentially no vertical gradient observed between July and early August, and then a slight downward gradient observed over the remaining portion of the year. The data collected during the second half of 2009 along the southern transect show that during episodic increases in the river elevations, surface water may be discharging into the aquifer. Otherwise there is primarily an upward gradient on both sides of the wall that may be associated with high-grade recovery operations.

2.5.2 GROUNDWATER, HYPORHEIC, AND SURFACE WATER MONITORING

The groundwater, hyporheic, and surface water monitoring wells were purged and sampled using a low flow methodology to prevent potential disturbance of the water quality. An inflatable packer system was used within the hyporheic/surface water zone monitoring wells to isolate a one foot interval within the uppermost portion of the water column to collect the surface water sample, and then to isolate a portion of the screen at the surface water/groundwater interface to collect the hyporheic water sample. Samples collected from the barrier monitoring network during September and December 2009 were analyzed for the dissolved phase constituents of concern. In addition, samples collected from the middle and southern transects in December 2009 were also analyzed for natural attenuation indicators. Field forms from these monitoring events are provided in Appendix C. Groundwater, hyporheic zone, and surface water analytical reports and data validation reports are included in Appendix D.

A summary of the groundwater results for constituents of concern and natural attenuation parameters are provided on Tables 2-5a and 2-5b. There were low level concentrations of ethylbenzene and total xylenes measured in samples collected from BSW-1S, BSW-2S, BSW-2D, BSW-3S, and BSW-3D during the September and December 2009 monitoring events. The samples designated with an “S” indicate a surface water sample and those designated with a “D” indicate hyporheic water samples. These constituents were not detected in the inboard monitoring wells or other wells on the outboard portions of the wall indicating the source was not associated with petroleum hydrocarbons present in the smear zone along the west bank of the river.

In addition, toluene was reported in the groundwater sample collected from well MW-137I at an estimated concentration of 0.0007 mg/L below the laboratory detection limit in September 2009 and dissolved phase arsenic was reported in the samples collected from well MW-136S in September and December 2009 at a concentration of 0.0238 and 0.0215 mg/L, respectively. There were no corresponding detections in the outboard monitoring wells. The surface water screening standards were not exceeded in any of the hyporheic or surface water samples collected during the second half of 2009.

2.6 VAPOR MONITORING

Soil vapor sampling from the nested monitoring wells is conducted as part of the routine monitoring program associated with the final corrective measures program to: (1) confirm that there is not a risk to residents in Hooven associated with intrusion of volatile constituents present in soil vapor that are associated with releases from the former refinery, (2) track remedial system effectiveness on reducing the concentration of petroleum related constituents present in the deep portions of the vadose zone, and (3) estimate the mass of petroleum hydrocarbons that are attenuated within the smear zone over the course of the final groundwater remedy. There were three soil vapor monitoring events conducted in Hooven and the Southwest Quad during 2009. Table 2-6 provides a summary of soil vapor samples collected from the nested vapor monitoring wells during each of these events. The following is a brief summary of each event.

- Soil vapor samples were collected from nested well VW-96 between March 4 and 5, 2009 as part of additional investigation activities conducted near this well. Soil vapor samples were collected from each of the intervals in this well during sampling performed in March 2009.
- Soil vapor samples were collected from newly installed nested vapor monitoring well VW-139 on July 1 2009. This monitoring well was installed above the smear zone in the Southwest Quad in fulfillment of the *Soil Vapor Profile Investigation Work Plan for Southwest Quad, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro

2009c). Samples were collected from each of the intervals in this nest with the exception of the 40-foot interval which was submerged beneath the water table.

- Sampling was performed in nested wells VW-93, VW-96, VW-99, VW-127, VW-128, VW-129, VW-130, and VW-139 between September 29 and October 2, 20010. This monitoring event was performed as part of a comparative study to the vapor intrusion (VI) investigation conducted by the USEPA Superfund Technical Assessment and Response Team (START) at the request of the Ohio Department of Health (ODH). Soil vapor samples were collected from each of the vapor monitoring probes installed in the nested vapor monitoring wells during this event with the exception of the 10-foot probe in well VW-99A, which is a redundant probe; and the 50-foot probe in well VW-130, which was installed within the upper portions of the bedrock.

Field forms for the vapor monitoring activities conducted 2009 are provided as Appendix F. Laboratory analytical reports for the soil vapor samples collected during each of these events are provided in Appendix G-1 and data validation reports for each of the analytical packages provided by the laboratory are included in Appendix G-2.

2.6.1 STATIC VACUUM/PRESSURE

Prior to initiating sampling activities, the static pressure or vacuum within the nested soil gas probes was assessed to determine whether there were any gradients that might induce soil gas flow. A summary of the static pressures or vacuums measured in the nested soil gas probes during the monitoring event conducted during 2009 is provided on Table 2-7. In general, the initial static pressure or vacuum measurements were between 0.00 and 0.5 inches of water, which is in the range that can be produced from wind and barometric pressure. The following anomalies were noted in the initial vacuum and pressure measurements during the soil vapor monitoring events completed in 2009:

- An elevated vacuum measurement (-1.79 inches of water [in-H₂O]) was observed in the 35 foot interval in nested well VW-93 in September 2009.
- Probes installed from 10 to 25 ft-bgs in VW-96 were measured with elevated vacuums during the monitoring performed in October 2009 that may be explained by decreasing water levels and pore water drainage during these events.
- A vacuum of -0.91 inches of water was measured at the 5 foot interval in well VW-99 during monitoring performed in early October 2009.
- An elevated vacuum was measured in the 5, 10, and 15 ft-bgs probes installed in nested well VW-127 in October 2009.

- In July 2009, a pressure of 3.73 inches of water was measured in the 40 foot probe in nested well VW-139. This probe was submerged beneath the water table during this monitoring event.
- An anomalously high vacuum of -12.76 inches of water was recorded in the 5 foot interval of nested well VW-139 during the September/October 2009 event. This would represent a significant enhanced vacuum and soil vapor would be advectively drawn towards the shallowest interval in this well. In July 2009, a static vacuum of 0.01 inches of water was measured in this same interval. It is believed that the September/October 2009 measurement is invalid.

For many of these measurements the cause of the measured vacuum is not known but would indicate preferential flow of soil gas towards this interval during these events. The HSVE system was not operated between December 2007 and October 2009 per USEPA requirements during their independent VI investigation in Hooven. Therefore, any elevated vacuum measurements are not attributable to residual effects from the HSVE system, but more likely associated with water table fluctuations unless otherwise noted.

2.6.2 SOIL GAS PERMEABILITY

Pneumatic testing was performed at each probe by measuring the differential pressure over increasing soil vapor extraction rates. The gas permeability of geologic materials around the nested soil gas probes was estimated using data collected through pneumatic testing and is included on Table 2-7. Soil gas permeability within the nested probes were primarily between $1\text{E-}7$ to $1\text{E-}8$ square centimeters (cm^2) with specific capacities (flow rate per unit of vacuum applied) ranging from 2.7 to 49 cubic centimeters per second per inch of water column ($\text{cm}^3/\text{sec}\cdot\text{in-H}_2\text{O}$), which are typical for medium to coarse grained sands. Soil gas permeability in the 30 and 40-foot interval in soil vapor monitoring well VW-127 and the 10 and 15-foot interval within nested well VW-129 were estimated at $1\text{E-}9$ cm^2 with specific capacities of approximately 1.5 $\text{cm}^3/\text{sec}\cdot\text{in-H}_2\text{O}$, which are representative of finer grained sands. Whereas, soil gas permeability in the 60-foot interval in nested vapor monitoring well VW-93 was estimated at $1\text{E-}5$ cm^2 indicative of coarse sand and gravel deposits.

2.6.3 NESTED SOIL GAS ANALYTICAL RESULTS

A summary of the soil vapor analytical results for the deep nested monitoring wells is provided on Table 2-8. This includes soil vapor monitoring results dating back to 1997. The target analytes have been divided into four classes on these tables including: (a) petroleum related constituents, (b) solvent related constituents, (c) water treatment related and other constituents, and (d) fixed gases.

2.6.3.1 PETROLEUM RELATED CONSTITUENTS

During monitoring performed in March 2009, seven of the 25 petroleum related constituents were detected in samples collected from nested well VW-96. Seven petroleum related constituents were also reported in the samples collected from well VW-139 during monitoring in July 2009. Finally, 18 of the 25 petroleum related constituents were detected during the September/October 2009 event.

The highest concentrations of petroleum related constituents were detected within the samples collected from the 55 and 60 foot intervals of nested well VW-96, the 50 and 55 foot intervals of well VW-99, and the 40 foot interval in nested well VW-139. These intervals are situated within the smear zone associated with releases from the former refinery and are representative of the vapor source. Concentrations of petroleum related compounds in the samples collected within the vapor source from wells VW-96 and VW-139 were higher during the September/October 2009 monitoring events compared to the March and July events, as the water table decreased and lower portions of the smear zone were exposed during high-grade recovery. In addition, the HSVE system was not operated in the 22 months preceding this event.

In the remainder of the probes above the vapor source in nested wells VW-96 and VW-99 concentrations of petroleum related constituents increased during 2008 and 2009. Historic soil vapor data collected from nested well VW-96 and VW-99 have indicated an alternate source of volatile petroleum hydrocarbon vapors in the shallow and intermediate portions of the vadose zone near these two wells. Soil vapor monitoring results have not indicated alternate shallow sources of petroleum hydrocarbons near nested well VW-93 or near newly installed nested well VW-139, located above the smear zone in the Southwest Quad. Additional subsurface assessment activities conducted in March 2009 to evaluate the nature of the alternate sources near nested well VW-96 included: 1) the installation of several soil borings and collection of cores for laboratory analysis of volatile and semivolatile organic constituents at target intervals based on physical observations and total organic vapor measurements, 2) installation of ROST borings adjacent to vapor well VW-96, and 3) collection of soil vapor samples for field screening of fixed gases during three additional monitoring events. The results of this assessment confirmed alternate petroleum related sources in the intermediate and shallow portions of the vadose zone near nested well VW-96 that were unrelated to petroleum hydrocarbons in the smear zone associated with releases from the former Gulf Refinery. Results of these assessment activities were submitted to the USEPA on September 14, 2009 via the letter report titled, *Subsurface Assessment Adjacent to MW-96 Results Summary, Chevron Cincinnati Facility, Hooven, Ohio* (Chevron 2009). This letter report was updated following installation of additional ROST borings in December 2009 (Chevron 2010a). A discussion of the lines of evidence

supporting the affects of alternate sources of petroleum hydrocarbons on the soil vapor conditions near nested wells VW-96 and VW-99 is provided within the *Hooven Vapor SCM Update* (Trihydro 2010).

During monitoring conducted between September/October 2009 in nested wells VW-93, VW-128, VW-129, and VW-130, petroleum related constituents were reported intermittently within the samples collected from these nested wells at low concentrations. Samples collected from nested well VW-139 showed elevated concentrations of petroleum related constituents within the vapor source located at approximately 40 ft-bgs that rapidly attenuated to background and non-detect concentrations by the 30 foot interval. It is expected that if alternate sources were not present near nested vapor wells VW-96 and VW-99, the concentrations of petroleum hydrocarbons within the intermediate and shallow portion of the vadose zone near these locations would be expected to be similar to those observed in nested well VW-139, as well as historical results (1997 through 1999) from well VW-93.

2.6.3.2 SOLVENT RELATED CONSTITUENTS

There were 12 solvent related chemicals detected during monitoring conducted during 2009. Acetone, 2-butanone, and isopropanol were the most frequently detected solvents in the soil vapor samples collected from the nested wells with an overall frequency of detection of approximately 53%, 46%, and 16%, respectively. Acetone, 2-butanone, and isopropanol are ubiquitously used for residential and commercial purposes within structures and are also considered common laboratory contaminants as they are used for cleaning and preparation of samples within the laboratory. The solvents were detected at a higher frequency in soil gas samples collected from locations outside of the distribution of petroleum related impacts attributed to the former refinery as a result of elevated reporting limits for samples collected from wells VW-96 and VW-99. The detection limits were raised by the laboratory for samples collected from these two wells as a result of elevated concentrations of petroleum related constituents during 2009.

Tetrachloroethene was only reported in samples collected from 15 to 50 ft-bgs in nested well VW-127 during the September/October 2009 monitoring event. Additionally, 1,1,1-trichloroethene was reported in six of the eight samples collected from monitoring well VW-129, situated outside of the smear zone and dissolved phase impacts. In addition, acetone, 2-butanone, and isopropanol were measured continuously in vapor samples collected from the deepest intervals to the shallowest soil vapor probe within from nested well VW-139 during the July 2009 monitoring event. These measured solvent related constituents are not associated with releases from the former refinery and are indicative of alternate sources of volatile constituents beneath Hooven and the Southwest Quad.

2.6.3.3 WATER TREATMENT RELATED AND OTHER CONSTITUENTS

Nine of the 22 water treatment related and other chemicals were detected during the monitoring performed in 2009. During the September/October event, dichlorodifluoromethane was reported in all of the samples collected from wells VW-128, VW-129, and VW-130 with the exception of the shallowest probe in well VW-128. In addition, trichlorofluoromethane was reported in the soil gas samples collected from each of the intervals in nested wells VW-129. Nested wells VW-129 and VW-130 are located in the central and western portions of Hooven outside of the distribution of LNAPL and dissolved phase constituents associated with the refinery, suggestive of an alternate source for these two constituents. Dichlorodifluoromethane and trichlorofluoromethane were historically used as freon within refrigerants and are ubiquitous in the environment. Freon use decreased in the 1980's after federal regulatory agencies banned their use because of their detrimental effects on the ozone layer. Freons are commonly detected at elevated concentrations beneath landfills due to improper disposal practices.

2.6.3.4 FIXED GASES

Fixed gas concentrations including O_2 , CO_2 , and CH_4 were measured during purging of the nested probes to determine that steady state conditions had been achieved prior to the collection of the soil gas sample for laboratory analysis and as a quality assurance/quality control measure of the analytical results. Field screening results indicated that the fixed gas measurements were generally stable prior to collecting samples from the nested soil vapor wells. The fixed gas measurements are included on the field forms provided in Appendix F.

The O_2 and CO_2 analytical results for the soil gas samples are summarized on Table 2-8d. The O_2 and CO_2 concentrations recorded in the field can be compared to the fixed gas results provided by the laboratory as a measure to validate the field results. Correlation plots showing the field reported O_2 and CO_2 concentrations and the laboratory analytical data for samples collected from the nested wells in September/October 2009 are provided as Figure 2-11. During this event, O_2 and CO_2 concentrations reported in the field were generally comparable to the laboratory reported results. There was some significant deviation in the laboratory reported and field measured O_2 and CO_2 concentrations for selected intervals during the September/October 2009 monitoring event that may be associated with elevated CH_4 observed within these soil vapor samples.

During sampling conducted between 2008 and 2009, O_2 was consumed in shallower and shallower portions of the vadose zone near nested wells VW-96 and VW-99, which in turn limited diffusion of O_2 into deeper portions of the vadose zone, thereby reducing the rate of aerobic degradation of the source at depth. This consistent trend towards anaerobic conditions (O_2 below 2% and elevated CH_4 concentrations) near these two wells is associated with extended

shut down of the HSVE system combined with a decreasing water table, in addition to alternate sources of petroleum related chemicals present in the shallow and intermediate portions of the vadose zone. During the September/October 2009 monitoring event this was magnified by artificially depressing the water table and exposing the lower portions of the smear zone via high-grade pumping.

O₂ transport to the deep portions of the vadose zone near nested wells VW-93 and VW-139 was not rate limited due to the presence of alternate hydrocarbons within shallow and intermediate portions of the vadose zone. O₂ was able to diffuse into deeper portions of the vadose zone resulting in significant reduction of hydrocarbon concentrations to non-detect or background levels within 10 feet above the smear zone. If alternate sources were not present near nested vapor wells VW-96 and VW-99 the O₂ concentrations within the vadose zone at these would be expected to be similar to those observed at nested wells VW-93 and VW-139.

2.6.4 OUTDOOR AIR ANALYTICAL RESULTS

A single “floating” outdoor air canister was collected each day soil vapor monitoring was performed in 2009. The ambient air samples were collected using a 6-liter Summa canister suspended approximately five feet above the ground surface using a flow-controller calibrated to collect the sample over an eight hour period. This “floating” sample remained secured outdoors and the Summa canister was open, collecting a sample, while the team was engaged in soil vapor monitoring activities. The Summa canister was shut, and not collecting a sample, during transport or when sampling activities were not being conducted.

Outdoor air analytical results are summarized on Table 2-9. Both petroleum and non-petroleum related constituents were detected at low concentrations in the outdoor air samples. Acetone, benzene, 2-butanone, chloromethane, dichlorodifluoromethane, ethanol, isopropanol, toluene, and trichlorofluoromethane were detected in nearly every sample.

The outdoor air constituent concentrations reported for the 2009 monitoring events were compared to the 50th percentile values from the *Summary of Indoor and Outdoor Levels of Volatile Organic Compounds from Fuel Oil Heated Homes in New York State* (NYDOH 2005). These average outdoor air concentrations are included on Table 2-9. The reported results for the outdoor air samples were generally within the range of the average ambient air data with the exception of concentrations of acetone, 2-butanone, chloromethane, ethanol, dichlorodifluoromethane, and trichlorofluoromethane, which were detected at concentrations an order of magnitude greater than the published

average outdoor air concentrations. These compounds are not petroleum related constituents. The reported concentrations are indicative of an alternate, ambient source of impacts in outdoor air during sampling.

2.6.5 METEOROLOGICAL DATA

A full scale weather monitoring station, located at the Chevron Cincinnati Facility was utilized in combination with the National Oceanic and Atmospheric Administration (NOAA) records to acquire meteorological data during monitoring performed in 2009. Meteorological data, including ambient temperature, barometric pressure, precipitation, wind speed, and wind direction was automatically logged during sampling activities. Appendix H presents hourly meteorological data logged on 10-minute intervals during the second 2009 monitoring event.

3.0 INTERPRETATION

Data collected during the second half of 2009 and included herein continue to demonstrate that the intrinsic processes in the saturated and unsaturated zones are degrading petroleum hydrocarbons in the smear zone. In general, natural attenuation occurs as constituents present in the smear zone partition to groundwater and soil vapor, where they are biodegraded via aerobic and anaerobic processes. There are two general lines of evidence provided herein to support the efficacy of natural attenuation processes to degrade petroleum hydrocarbons at a rate that will achieve remedial goals for groundwater (i.e. USEPA maximum contaminant levels) in a timeframe comparable to active remedial measures. The primary lines of evidence demonstrate the stability of petroleum hydrocarbons in the smear zone beneath the Site and protectiveness of sensitive receptors (Section 3.1); as well as meaningful trends of decreasing constituent concentrations over time (Section 3.2). The secondary lines of evidence, discussed in Section 3.3, include evaluation of hydrogeochemical data that demonstrate indirectly the natural attenuation mechanisms acting to transform hydrocarbon constituents, reduce concentrations, and inhibit mobility of the LNAPL, dissolved phase, and vapor phase impacts. Baseline qualitative and quantitative lines of evidence were discussed in the *First 2008 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2009a). Updates to these lines of evidence for which data was collected during the second half of 2009 are included herein.

3.1 PLUME STABILITY AND PROTECTIVENESS OF SENSITIVE RECEPTORS

During execution of the final groundwater remedy at the Site, Chevron must continue to demonstrate that the LNAPL and dissolved phase plumes are stable and that sensitive receptors remain protected (USEPA 1999). If the extent of the LNAPL, dissolved, or vapor phase petroleum hydrocarbons are determined to be mobile or impacting sensitive receptors above risk based limits, contingency measures would be employed as outlined in the *OMM Plan* (Trihydro 2007b).

3.1.1 LNAPL

As discussed in the *Update to Site Conceptual Model and Summary of Remedial Decision Basis* (Chevron Cincinnati Groundwater Task Force 2005) and outlined within the *First 2008 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2009a), LNAPL within the smear zone is stable. This determination was made based on (1) the age of the release; (2) a decrease in LNAPL gradients, transmissivity, and saturations due to natural degradation and engineered recovery; (3) morphology of the smear zone with a “thicker” core, which thins at the lateral edges; (4) there having been no expansion of LNAPL beyond the originally defined limits of the smear zone; and

(5) preferential depletion of petroleum related constituents within the LNAPL at the soil gas and groundwater interface (otherwise referred to as outside-in weathering of the plume).

Data collected during the second half of 2009 continue to support that the smear zone is stable based on the laser induced fluorescence measurements in the three ROST monitoring transects collected between December 16 and 18, 2009. Additionally, LNAPL was not measured in any of the sentinel or point of compliance monitoring wells installed in the Southwest Quad. Fluid level gauging within the performance monitoring network installed along the west bank of the Great Miami River also confirmed the stability of the smear zone along the restored river bank.

During high-grade recovery performed between August and December 2009, LNAPL was measured in monitoring wells MW-101S, MW-122, MW-125, and MW-128 as the water table was artificially depressed beneath Hooven. LNAPL is not observed within these wells during seasonal low water table conditions, when high-grade recovery is not being performed. LNAPL thicknesses were measured from as little as a few hundredths of a foot in monitoring well MW-128 to several tenths of a foot in well MW-125. These observations are consistent with the site conceptual model for plume stability described in Section 1.1.3; the LNAPL and dissolved phase limits are generally coincident at the up-gradient and lateral edges of the smear zone with detection of dissolved phase petroleum hydrocarbons being indicative of LNAPL within the smear zone. The results of the high-grade recovery event conducted during the second half of 2009 are further discussed in Section 4.0.

Historical petrophysical tests on soil cores collected in the saturated portions of the smear zone indicate two-phase (water-oil) LNAPL residual saturation ranges from about 18 to 25%. Data collected from the facility show an exponential decrease in the ability of LNAPL to migrate at saturations below 20 to 25%. Field testing completed in the late 1990s indicates that the two-phase LNAPL saturations in the majority of the plume were below residual values (i.e., immobilized). Additionally, soil core samples were collected on the facility in November 2008 and soil saturations calculated using this data also demonstrated that LNAPL saturations within the upper, middle, and lower portions of the smear zone were below residual values.

Smear zone coring was completed in May 2009 in Hooven near monitoring wells MW-93 and MW-96 and the LNAPL saturations were estimated using the total petroleum hydrocarbon concentrations averaged for the soil cores collected at each location, soil bulk density, LNAPL density, and soil porosity. The total petroleum hydrocarbon concentrations for smear zone location SZ-93, as well as the upper and middle location at well SZ-96 indicate that petroleum hydrocarbons are sorbed to soil or present in the dissolved phase, and LNAPL is no longer present. Average LNAPL

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saturations in the lower portion of the smear zone near monitoring well MW-96 was 5.6%. As with the saturations measured within the soil cores collected on the facility in November 2008, the LNAPL saturations in Hooven were below the residual values and the plume is considered immobile.

3.1.2 DISSOLVED PHASE

As previously described in Section 2.2.1, benzene was detected in the groundwater sample collected from sentinel well MW-35 during routine monitoring conducted in November 2008 at a concentration of 0.13 mg/L, which exceeded the MCL (0.005 mg/L). None of the other volatile constituents of concern (ethylbenzene, toluene, xylenes, or chlorobenzene) were detected above laboratory detection limits in samples collected from well MW-35 or any of the other sentinel or POC wells during sampling conducted in November 2008.

Sentinel well MW-35 and the corresponding down-gradient POC well MW-133 along with wells MW-131 through MW-134 were re-sampled between February 17 and 19, 2009 for the dissolved phase constituents of concern. Benzene was reported in the groundwater sample collected from well MW-35 at a concentration of 0.021 mg/L, in addition to the sample collected from the POC well MW-133 at an estimated concentration of 0.003 mg/L. Again, there were no other detections of the volatile constituents of concern within any of the other wells. Although the source of the dissolved phase benzene was not believed to be associated with historical releases from the refinery present in the smear zone, hydraulic containment pumping was resumed in late March 2009. Containment pumping using production wells PROD_15 and PROD_24 continued until August 2009 when high-grade recovery was initiated.

During routine monitoring conducted in the second half of 2009, none of the constituents of concern were measured in any of the other sentinel or POC wells installed in the Southwest Quad. Benzene has not been measured above detection limits in samples collected from sentinel well MW-35 since March 2009, while benzene persisted in groundwater samples collected from POC well MW-133 until August 2009. As described in the *Work Plan for Contingency Measures in the Southwest Quad, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2009d), there are several lines of evidence indicating that the dissolved phase benzene detected in sentinel well MW-35 and POC well MW-133 is associated with alternate sources within the Southwest Quad. Thus, the detections of benzene are not believed to be associated with re-distribution of petroleum hydrocarbons associated with the former refinery and the dissolved phase plume is concluded to be stable beneath the Southwest Quad.

3.1.3 VAPOR PHASE

In order to evaluate protectiveness of human health from migration of deep soil vapors into structures located in Hooven, the data from the nested wells is compared to the conservative risk based screening standards. Screening standards are concentrations that are sufficiently low that any results below these can safely be considered to pose no significant risk. Screening standards are developed with consideration for uncertainty, and are designed to be overly protective; therefore, concentrations above the screening levels do not necessarily pose an unacceptable risk.

Table 3-1 provides the screening level evaluation for the deep soil gas samples for gasoline related constituents. The residential indoor air screening levels (assuming a lifetime incremental cancer risk of $1\text{E-}5$ for carcinogenic constituents and a Hazard Quotient of 1 for non-carcinogenic constituents) provided on the USEPA Regional Screening Level (RSL) tables (USEPA 2009a) were divided by semi-site specific attenuation factors from Figure 3a of the USEPA OSWER *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils* (OSWER *Draft VI Guidance*, USEPA 2002) to derive soil vapor screening levels (SVSLs). This approach for defining the SVSLs was developed in cooperation with USEPA Region V risk assessment staff and has been presented in previously submitted semiannual monitoring reports (Trihydro 2009a, b, e). Application of the attenuation factors from Figure 3a of the *OSWER Draft VI Guidance* is extremely conservative for this evaluation, since these do not account for attenuation due to aerobic biodegradation, which is the chief mechanism limiting vapor transport beneath Hooven.

The 2009 residential RSLs are used to define the SVSLs, as these were developed with the updates to the toxicity data for inhalation of many petroleum and non-petroleum related constituents, and as such represent the most current understanding of the health effects of inhaling the petroleum related constituents discussed herein. In December 2009, the USEPA Office of Inspector General identified that the indoor air screening levels provided in the *OSWER Draft VI Guidance* were outdated and may impede evaluation of the VI pathway (USEPA 2009b). In general, the RSLs are comparable or lower (more protective) than the screening levels provided within the *OSWER Draft VI Guidance*, with the exception of toluene, hexane, and 1,3-butadiene, which were higher. Four constituents (the alkylbenzenes [n-propyl-, n-butyl-, and sec-butyl-] and methylcyclohexane) had screening levels in the *OSWER Draft VI Guidance* for which the USEPA did not calculate RSLs, as the most recent toxicity data did not support inclusion of these constituents as an inhalation risk.

It is worth noting that screening levels were not provided in the *OSWER Draft VI Guidance* or included as part of the RSL tables for 2,2,4-trimethylpentane. 2,2,4-trimethylpentane is a major component of gasoline and has been detected

in soil gas samples collected from the vapor source above the smear zone since 2005. In July 2007, the USEPA summarized the available hazard and dose-response assessment information for 2,2,4-trimethylpentane in the document titled *Toxicological Review of 2,2,4-Trimethylpentane* (USEPA 2007). This report is intended as a thorough review of the scientific understanding regarding the toxicology of 2,2,4-trimethylpentane with the stated purpose of providing “scientific support and rationale for hazard and dose-response assessment in the Integrated Risk Information System pertaining to chronic exposure.” In other words, it specifically addressed the task of developing defensible reference concentrations (rfCs) and reference doses (rfDs) for chronic exposure to 2,2,4-trimethylpentane. This report was prepared by independent toxicologists, and was subjected to peer review by both USEPA-internal and external toxicologists prior to finalization. The final version reflects an achieved common understanding among the multiple USEPA branches and concludes that there is insufficient data to develop defensible rfCs or rfDs for 2,2,4-trimethylpentane. As such, a screening evaluation for 2,2,4-trimethylpentane is not provided herein.

The screening level evaluation was applied to the deep soil vapor samples collected from 20 ft-bgs or greater in Hooven. The data collected from the shallow probes was not evaluated because vapor concentrations at depths less than 20 ft-bgs are attributable to alternate, surface derived sources of petroleum hydrocarbons. Based on Figure 3a of the *OSWER Draft VI Guidance*, an attenuation factor of 0.002 was applied to samples collected from depths of 20 ft-bgs, 0.001 was used to screen soil vapor data from greater than 20 ft-bgs to 35 ft-bgs, and an attenuation factor of 0.0007 was used to screen data greater than 35 ft-bgs. Note that the attenuation factors shown on Figure 3a of the *OSWER Draft VI Guidance* correspond to the depth below the foundation. For this evaluation the depth of the basement was conservatively assumed to be 5 ft-bgs; therefore, a sample depth of 20 ft-bgs corresponds to a depth of 15 feet, as shown on Figure 3a.

A similar screening level approach was applied for petroleum related vapors measured in nested vapor well VW-139, with the significant exception that structures within the Southwest Quad have a slab-on-grade foundation. The SVSLs for the Southwest Quad were calculated using the RSLs for residential air and semi-site specific attenuation factors from Figure 3a of the *OSWER Draft VI Guidance*. For depths between 5 and 10 ft-bgs an attenuation of 0.002 was used, for depths of greater than 10 ft-bgs to 30 ft-bgs an attenuation factor of 0.001 was used, and for depths greater than 30 ft-bgs an attenuation factor of 0.0007 was used. This is a conservative evaluation as ambient background concentrations were not accounted for in the shallow vapor samples collected from well VW-139 and there are no residences situated within the Southwest Quad.

During 2009 soil vapor samples have been collected from vapor nests VW-93 (1 event), VW-96 (2 events), and VW-99 (1 event) over the smear zone in Hooven, as well as nest VW-139 (2 events) situated above the smear zone in the Southwest Quad. Additionally, samples have been collected from vapor nests VW-127 and VW-128 (1 event), which are located over the dissolved phase petroleum hydrocarbons, and nested wells VW-129 and VW-130 (1 event) installed outside of the smear zone and dissolved phase petroleum hydrocarbons. There were no exceedances of the SVSLs in any of the samples collected from nested monitoring wells VW-93, VW-127, VW-128, VW-129, and VW-130. There were three exceedances of the SVSLs in the detected results from nested soil vapor monitoring wells VW-96, VW-99, and VW-139. Detected concentrations of benzene and ethylbenzene exceeded the depth-specific SVSL in the sample from the deepest interval (60 ft-bgs) in well VW-96. In addition, the detected concentrations of 1,2,4-trimethylbenzene exceeded the depth-specific SVSLs in the duplicate sample collected from the deepest interval in nested well VW-139. These probes were installed within the upper limits of the smear zone at these locations.

The detection limits for several constituents including 1,2-dichloroethane, 1,2-dibromoethane, 1,2,4-trimethylbenzene, 1,3-butadiene, 1,3,5-trimethylbenzene, benzene, ethylbenzene, hexane, and naphthalene exceeded the depth-specific SVSL in intervals reported with non-detect results within nested wells VW-96, VW-99, and VW-139 during the March and September/October 2009 sampling event. Typically samples collected from intervals within these nests were reported with non-detect results for these constituents below the SVSLs, while other intervals within the same nest had sample results that exceeded the SVSLs. This would indicate that the constituent concentrations were below conservative risk based levels within the vadose zone near these wells.

The reporting limits for 1,2-dichloroethane, 1,2-dibromoethane, 1,3-butadiene, 1,3,5-trimethylbenzene, benzene, and naphthalene exceeded the respective SVSLs throughout the intermediate and deep portions of the vadose zone in nested wells VW-96 and VW-99 during at least one of the monitoring events performed in 2009. Such cases include:

- 1,2-dichloroethane in samples collected from nested wells VW-96 and VW-99 in September/October 2009
- 1,2-dibromoethane in samples collected from nested well VW-96 in March 2009 and September/October 2009, as well as nest VW-99 in September/October 2009
- 1,3-butadiene in samples collected from nested wells VW-96 and VW-99 in September/October 2009
- 1,3,5-trimethylbenzene in samples collected from nested well VW-96 in September/October 2009
- Benzene in samples collected from nested well VW-96 in September/October 2009
- Naphthalene in samples collected from nested wells VW-96 and VW-99 in September/October 2009

Though the data from wells VW-96 and VW-99 for the dates listed above are insufficient to determine that these constituents were not present above the SVSLs, the monitoring results combined with historical data provide some insight into the VI pathway at these locations. First, there were no detected concentrations of these constituents above their respective SVSLs, even in samples collected in the deepest samples within the smear zone for most of these constituents with the exception of benzene. In addition, data collected during previous monitoring events indicate that the VI pathway was incomplete for these constituents. Finally, for constituents that were detected in the deepest sampling intervals above SVSLs (benzene, ethylbenzene, and 1,2,4- trimethylbenzene), the analytical results strongly supports rapidly decreasing concentrations within shallower depths above the smear zone. The data collected in 2009 continues to demonstrate that there is not a risk to residents in Hooven, students or teachers in the elementary school, or occupants of businesses associated with intrusion of volatile constituents associated with releases from the former refinery.

3.2 CONSTITUENT TRENDS

It is expected that the data collected over the course of the remedy will show a meaningful trend of decreasing hydrocarbon mass and/or constituent concentrations over time. Analyses that may be used in evaluating the progress of the long term remedy in meeting remedial goals (i.e., MCLs in groundwater) include evaluation of temporal trends in contaminant concentrations, LNAPL mass, or LNAPL saturations; comparisons of observed contaminant distributions with predictions; as well as comparison of calculated attenuation rates with those necessary to meet remedial goals within the required time frame. These analyses can be complicated as a result of variation in the petroleum hydrocarbon distribution across the site, temporal fluctuations related to seasonal and longer term trends, heterogeneity in the vadose and saturated zones across the plume footprint, along with measurement variability. These complications necessitate the use of multiple lines of evidence and expanded monitoring networks to reduce uncertainty.

3.2.1 LNAPL AND SOIL CORE CONSTITUENT TRENDS

Figure 3-1 shows the mole fraction of benzene in LNAPL samples collected in 1997, 1999, and 2005 from four sets of wells (MW-1R/PROD_20, MW-58/PROD_12, PROD_15, and MW-96S) on a logarithmic-linear scale. This figure also shows the decline in the average benzene mole fraction for all the LNAPL samples collected over this timeframe. The trends presented on this figure depict a first order degradation rate for benzene in the LNAPL since 1997.

As the LNAPL saturation and transmissivity continue to decrease across the smear zone over time, it may become infeasible to collect LNAPL samples for laboratory analysis. As a result, smear zone soil coring will be conducted to

provide a means of measuring LNAPL composition, with the first coring events performed in 2008 and 2009. The benzene mole fractions estimated within the soil cores collected during these initial events were compared to the benzene mole fraction in LNAPL shown on Figure 3-1. There was general agreement between benzene mole fractions reported in the LNAPL samples collected in 2005 and smear zone soil cores collected in 2008 and 2009, with slightly higher concentrations estimated in the soil cores. This is likely a function of the conservative assumptions used in calculating benzene mole fraction in LNAPL from the soil core samples.

It is important to note that the TPH concentrations measured in the soil core samples collected at boring SZ-93, as well as the top and middle samples collected at the locations SZ-96 were below 100 mg/kg. These low values are typically associated with petroleum hydrocarbons present in the dissolved phase, and sorbed to soil organic matter, rather than being present as LNAPL. The average TPH concentration measured in bottom samples collected at location SZ-96 was 3,055 mg/kg. This corresponds to a LNAPL saturation of approximately 5.6% (API Interactive LNAPL Guide, version 2.0.4, 2004).

In the past, LNAPL has been observed to enter monitoring wells MW-93 and MW-96. Under equilibrium conditions, LNAPL presence in a monitoring well would correspond to LNAPL presence in the formation near the water table. However, based on the TPH data, currently LNAPL is only present at the base of the smear zone near monitoring well MW-96, and absent near monitoring well MW-93. This suggests that environmental dynamics, such as a fluctuating water table, high grade LNAPL recovery, and HSVE operation, have acted to remove much of the subsurface LNAPL in these portions of Hooven. Future monitoring of the smear zone in Hooven will focus on the bottom sampling interval at location SZ-96, where LNAPL is still present. Smear zone soil coring will be conducted on five year intervals.

3.2.2 DISSOLVED PHASE CONSTITUENT TRENDS

The distribution of total benzene, toluene, ethylbenzene, and xylenes (BTEX) in groundwater as well as total petroleum hydrocarbons concentrations for samples collected during the second 2009 semiannual monitoring period are displayed on Figure 3-2. It is useful to evaluate the dissolved phase constituent trends in two ways. First, dissolved phase constituent trends within individual groundwater monitoring wells can be used to assess spatial variability in engineered mass removal and intrinsic biodegradation processes across the smear zone footprint and identify areas that are not behaving as predicted. Second, groundwater quality trends can be averaged within areas of the smear zone (i.e., up-gradient, interior, down-gradient) to assess overall trends in natural attenuation processes. For discussion purposes,

there are two areas up-gradient of the smear zone, one to the north of the facility property and the second to the west along the Buried Valley Aquifer-bedrock interface in Hooven.

3.2.2.1 TRENDS WITHIN INDIVIDUAL MONITORING WELLS

While useful for inferring source zone depletion of individual constituents, temporal trends observed in the dissolved constituent concentrations collected from individual wells can also be essential indicators of plume stability and progress toward meeting remedial goals. In the absence of remedial efforts, (i.e. HSVE system operation), decreasing dissolved phase concentrations over time within the plume area indicate that natural attenuation processes are acting to reduce contaminant mass and concentrations. Trend analyses should be conducted in monitoring locations situated throughout the distribution of petroleum hydrocarbons to assess the range of dominant intrinsic processes acting on the plume. Temporal trends in individual wells may also indicate changes in climatic, hydrogeochemical, contaminant release, site reuse, or other conditions unrelated to attenuation processes and need to be evaluated in the context of other lines of evidence.

Historically, groundwater samples have not been collected from the interior plume monitoring wells due to the presence of LNAPL during sampling. For the purpose of this analysis, trends are inferred for wells that have groundwater data from at least three monitoring events spanning three separate years. Of the ten interior plume wells, six monitoring wells (MW-10, MW-18R, MW-20S, MW-58S, MW-88, and MW-96S) do not have data that meet these criteria. Constituent of concern concentrations reported in the samples collected from interior monitoring well MW-85D were all reported below the remedial goals, which is expected as this well is screened in the deeper portions of the Buried Valley Aquifer, well below the vertical distribution of dissolved phase petroleum hydrocarbons. Dissolved phase trends for the four remaining interior plume monitoring wells (MW-17, MW-22, MW-81S and MW-93S) are provided on Figures 3-3 through 3-6. Monitoring well MW-17 is located in the interior of the smear zone, where dissolved phase benzene concentrations continue to be measured at concentrations above remedial goals. There is a slight decreasing trend in benzene concentrations over time. This decreasing trend may become more pronounced over time as the smear zone up-gradient of well MW-17 becomes depleted and attenuation continues from the “outside-in.” Monitoring well MW-22 is located north of well MW-17, closer to the up-gradient edge of the smear zone, and accordingly shows a stronger decreasing trend in benzene concentrations over time. Monitoring well MW-81S is situated in the southwest limit of Hooven adjacent to State Route 128 and MW-93S is located in the central portion of Hooven adjacent to the elementary school. Dissolved phase constituent concentrations in these two wells show a clear decreasing trend between 1996 and 2009. This trend is likely associated with startup of the groundwater production, LNAPL recovery, and HSVE systems between 1999 and 2000.

Of the eight supplemental groundwater monitoring wells (L-1RR, L-3R, MW-21, MW-33, MW-51, MW-64, MW-80, and MW-99), wells L-1RR, L-3R, MW-21, MW-33, MW-64, and MW-99S had sufficient data (i.e., results from at least three monitoring events spanning more than three years) to complete a trend analysis. The dissolved phase results for the constituents of concern reported in samples collected from well MW-33 have remained below MCLs over time.

As presented on Figures 3-7 through 3-11, dissolved phase benzene concentrations reported in supplemental monitoring wells L-1RR, L-3R, and MW-21 showed a first order degradation rate over time. These wells are generally located outside of the footprint of engineered remedial measures at the facility; therefore these decreasing trends are indicative of natural attenuation processes. The rate of decline in benzene concentrations is greater in well MW-21 compared to monitoring wells L-1RR and L-3R, as this well is located along the up-gradient edge of the smear zone. The dissolved phase benzene concentrations reported in samples collected from monitoring wells MW-64 (Figure 3-10) and MW-99S (Figure 3-11) also show decreasing trends over time. These two monitoring wells are located on the eastern and western edge of the smear zone, respectively, and also demonstrate preferential depletion of benzene along the smear zone margins (i.e., outside-in weathering).

Temporal analysis of the dissolved phase results can also be conducted for two additional monitoring wells (MW-85S and MW-115S) located within the distribution of hydrocarbons at the facility, as these wells have a sufficient monitoring history with concentrations above remedial goals. Figures 3-12 and 3-13 show decreasing trends in dissolved phase benzene concentrations over time in these two monitoring wells. Monitoring wells MW-85S and MW-115S are located outside the influence of historic remedial efforts along the Great Miami River and in the Southwest Quad, respectively. Trends within these two wells are considered indicative of natural attenuation processes.

The average first order degradation rate estimated using the dissolved phase analytical results from eleven monitoring wells (L-1RR, L-3R, MW-17, MW-21, MW-22, MW-64, MW-81S, MW-85S, MW-93S, MW-99S, and MW-115S) is approximately 6.7×10^{-4} per day. This compares well with the first order decay rates estimated based on trends in the benzene mole fraction in LNAPL. The average estimated first order decay rate for benzene in LNAPL, based on LNAPL and smear zone soil samples collected between 1997 and 2009, is 5.34×10^{-4} per day.

As additional dissolved phase data is collected, it will be possible to make meaningful decisions regarding the temporal trends across the distribution of hydrocarbons. Attenuation rates will be compared over time within individual wells installed across the plume and progress towards meeting the remedial goals will be further considered.

3.2.2.2 AVERAGE TRENDS ACROSS SMEAR ZONE

Table 3-2 provides the average dissolved phase constituent concentrations measured in the up-gradient, interior, and down-gradient portions of the smear zone during the second half of 2009. The average dissolved phase constituent and total petroleum hydrocarbon concentrations are indicative of ongoing natural attenuation processes, with preferential LNAPL depletion at the smear zone boundaries. The average dissolved phase benzene concentration was 0.005 mg/L in samples collected from the monitoring wells located in the two up-gradient areas while the average concentration of dissolved phase benzene within the smear zone was 0.496 mg/L. Down-gradient of the smear zone, the average benzene concentration was 0.005 mg/L. This indicates that attenuation processes such as dispersion, sorption, and biodegradation reduce the dissolved phase concentration, reduce mobility of the plume, and/or transform constituents of concern as the plume exits the smear zone.

The average dissolved phase benzene concentration trends for selected monitoring wells located in the up-gradient (MW-21 and MW-22), interior (L-1RR, L-3R, MW-17, and MW-18R), and down-gradient (MW-48S, MW-94S, and MW-115S) portions of the smear zone are presented on Figure 3-14. Dissolved phase concentrations reported during monitoring conducted in 2002, 2004, 2008, and 2009 are averaged for the up-gradient, interior, and down-gradient wells. Irrespective of the well locations, there is a decreasing trend in the dissolved phase benzene concentration reported between 2002 and 2009, indicative of benzene depletion from the smear zone. These decreasing trends are more pronounced at the margins of the smear zone compared to the interior portion of the plume. At its margins, the smear zone is thinner and LNAPL saturations are lower. In addition, as reported on Table 3-2, groundwater enriched in electron acceptors intercepts the smear zone north of the facility and again to the southeast of the Buried Valley Aquifer-bedrock interface in Hooven creating a situation whereby petroleum hydrocarbons including benzene are attenuated more quickly along the margins than within the interior of the smear zone. These observations are consistent with the expectation of outside-in attenuation of petroleum hydrocarbons within the smear zone.

As the up-gradient portion of the smear zone is depleted of petroleum hydrocarbons, the benzene removal rates from the interior portion of the smear zone will increase as outside-in weathering continues. It is anticipated that the dissolved phase benzene concentrations reported in monitoring wells L-1RR and MW-17 will show trends similar to those currently observed in wells MW-21 and MW-22. This may then be followed by a similar transition in the dissolved phase benzene trends observed in monitoring wells L-3R and MW-18R. Over time, it is expected that benzene concentrations in groundwater will continue to decrease across the smear zone, eventually reaching remedial goals (i.e., USEPA MCLs).

3.2.3 VAPOR PHASE CONSTITUENT TRENDS

As with temporal analysis of the dissolved constituents of concern, soil vapor results from samples collected above the LNAPL plume (i.e., vapor source) should be considered as a line of evidence to demonstrate the effectiveness of natural attenuation mechanisms to degrade the smear zone over time. Vapor source trend analyses will be conducted using data collected from soil vapor monitoring wells installed across the distribution of petroleum hydrocarbons to assess the rate of attenuation in various portions of the plume. The trends observed in the vapor source should be evaluated in the context of the other lines of evidence to identify secondary causes of variation such as seasonal fluid level fluctuations or longer term cyclical events such as droughts.

Monitoring wells VW-93, VW-96, and VW-99 have a sufficient monitoring history to complete temporal analyses and are located over the smear zone. Figures 3-15 through 3-17 show the concentration of benzene and total petroleum hydrocarbons reported in the vapor source in nested wells VW-93, VW-96, and VW-99 over the past decade. A first order degradation rate is observed in the vapor source concentration since 1997, with a two to five order of magnitude decrease in benzene and total petroleum hydrocarbon concentrations. This decrease in concentrations is partially attributable to operation of groundwater, LNAPL, and soil vapor recovery systems in Hooven beginning in 1999.

Reduction in the TVPH and benzene concentrations has been more significant in well VW-93 compared to wells VW-96 and VW-99. This may be an indication that operation of the HSVE system alone does not fully account for the reduction of petroleum related constituents in the smear zone. Alternate sources of petroleum hydrocarbons have not been observed in the soil vapor profiles from well VW-93; therefore O₂ transport and aerobic biodegradation is not limited within the deeper portions of the vadose zone near this well.

There was a significant increase in the TVPH concentrations in the vapor source (i.e., deepest sample) reported in wells VW-96 and VW-99 between September 2008 and October 2009 associated with extended shutdown of the HSVE system. This trend was magnified during the latest event by operation of the high-grade system. Induced depression of the water table during high-grade operation exposed the deepest portions of the smear zone containing the highest mole fraction of volatile petroleum hydrocarbons (Trihydro 2009b).

3.3 GEOCHEMICAL INDICATORS OF NATURAL ATTENUATION

Characterization of geochemical variations in the vadose and saturated zones provides evidence of the types of biodegradation processes that are thought to be attenuating petroleum hydrocarbons in the smear zone. Many of the processes attenuating hydrocarbons in the smear zone cannot be measured directly (e.g., biological transformation of

contaminants). However, the processes may cause changes in geochemical parameters, leaving an observable “footprint” that can be related qualitatively and quantitatively to the natural attenuation processes (National Research Council 2000). In general, geochemical species serve as electron acceptors and are reduced during microbial degradation (i.e., oxidation) of petroleum hydrocarbons.

3.3.1 DISSOLVED PHASE CONSTITUENTS

During microbial degradation of petroleum impacts, the dissolved O_2 concentrations steadily decrease until anaerobic conditions prevail. Once anaerobic conditions exist and multiple potential electron acceptors (i.e., oxidizers) are available, microorganisms preferentially use the electron acceptor that is thermodynamically most favorable. The general order of preference for anaerobic hydrocarbon biodegradation based on the Gibb’s energy of the reaction is:

- Denitrification (reduction of nitrate), with the eventual production of molecular nitrogen
- Reduction of manganese from Mn^{4+} to Mn^{2+}
- Reduction of ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+})
- Sulfate reduction, with eventual production of sulfide
- Reduction of carbon dioxide (CO_2) and generation of CH_4

These microbial processes generally segregate into distinct zones dominated by O_2 , nitrate, ferric iron, sulfate, and CO_2 reduction. Furthermore, given the different electron acceptors consumed and final products produced it is theoretically possible to differentiate the “zones” of microbial processes across the smear zone.

If dissolved O_2 is present in groundwater above 0.5 mg/L, then aerobic biodegradation of petroleum hydrocarbons is the dominant process. If dissolved O_2 concentrations are less than 0.5 mg/L, but nitrate concentrations exceed 1.0 mg/L, then denitrification dominates. Because nitrite is an unstable intermediate product of denitrification, the presence of measurable nitrite concentrations is indicative of nitrate reduction. If groundwater is deprived of dissolved O_2 , nitrate, and nitrite; but concentrations of ferrous iron are greater than 0.5 mg/L then iron reduction will be the dominant biodegradation process. If groundwater is depleted in ferrous iron but contains concentrations of sulfate above 1.0 mg/L and hydrogen sulfide above 0.05 mg/L, then sulfate reduction will be the predominant process. Finally, if the groundwater is depleted in all the electron acceptors and by-products, with the exception of CH_4 greater than 0.2 mg/L, then methanogenesis is the predominant process degrading petroleum hydrocarbons. When applied at a field scale this differentiation of microbial zones commonly encounters uncertainties as many of the by-products of

microbial metabolism (such as ferric iron, hydrogen sulfide, and CH_4) are readily transported down-gradient. Based on data collected in 2008 (Trihydro 2009b), sulfate reduction and methanogenesis account for more than 90% of smear zone natural attenuation within the saturated zone.

The spatial distribution of electron acceptors measured during the second 2009 semiannual monitoring period is displayed on Figure 3-18. Nitrate and sulfate concentrations were higher up-gradient of the smear zone compared to within the smear zone. Specifically, the average nitrate and sulfate concentrations in up-gradient groundwater, as provided in Table 3-2, were 4.30 and 76.6 mg/L, respectively. Sulfate and nitrate enriched water enters the smear zone with groundwater flowing from the north of the facility and bedrock-aquifer interface in the western portions of Hooven. The average sulfate concentration within the smear zone was 31.9 mg/L, while nitrate was not detected above the reporting limit within the smear zone. Sulfate was reported at elevated concentrations in well MW-93S (144 mg/L), where the smear zone has been depleted via interim and final groundwater corrective measures. Nitrate and sulfate concentrations did not show a marked rebound in the down-gradient portions of the smear zone, likely the result of the supply of hydrocarbons in groundwater being exhausted by biodegradation processes.

The spatial distribution of reduced species and attenuation by-products including dissolved iron, manganese, and CH_4 are depicted on Figure 3-19. The concentration of each of these oxidation by-products was higher within the smear zone compared to up-gradient and down-gradient conditions. As reported in Table 3-2, the average dissolved iron, manganese, and CH_4 concentrations up-gradient of the smear zone were 0.048, 0.111, and 0.015 mg/L, respectively. Average dissolved iron, manganese, and CH_4 concentrations within the smear zone were 8.86, 0.706, and 6.33 mg/L, respectively. The increase in the concentration of these biodegradation by-products indicates iron and manganese reduction, as well as methanogenic processes, are degrading petroleum hydrocarbons. Down-gradient of the smear zone dissolved iron, manganese, and CH_4 concentrations decrease to 1.47, 0.606, and 0.202 mg/L, respectively.

Figure 3-20 shows the concentration of dissolved phase benzene versus distance through the centerline of the smear zone with a comparison to sulfate, iron, and CH_4 concentrations. Dissolved phase manganese was not included on these distances versus concentration plots as previous estimates suggest manganese reduction represents less than 1% of the total smear zone mass loss in the saturated zone. Additionally, nitrate was not included on this figure as denitrification is only a significant mechanism for natural attenuation in the southern portions of the smear zone. As portrayed on Figure 3-20, iron and sulfate reduction, as well as methanogenesis primarily occur within 2,000 feet down-gradient of the smear zone boundary where available electron receptors are fully reduced. There is a rapid increase in benzene, CH_4 , and dissolved iron concentrations with an associated decrease in sulfate. Between the

northern and central portions of the smear zone there was a subsequent rebound in sulfate and corresponding decrease in benzene, iron, and CH_4 that is attributable to high-grade recovery occurring during the second half of 2009. High-grade recovery operations result in significant groundwater depressions and hydraulic gradients towards the operating production well(s). These inward gradients enhance electron receptor concentrations and increase aerobic degradation mechanisms within the interior portions of the smear zone.

3.3.2 VAPOR PHASE CONSTITUENTS

Aerobic degradation of hydrocarbon vapors occurs (often in a relatively thin zone) where the concentrations of O_2 and volatile constituents in the soil vapor are optimal for the growth of petrophillic bacteria. Aerobic degradation has the potential to reduce soil gas concentrations by several orders of magnitude, as long as the supply of O_2 is not rate limiting (Roggemans et al. 2001). CO_2 is produced as a result of aerobic biodegradation of hydrocarbons. The expected vertical profiles of O_2 and CO_2 concentrations in the presence of aerobic biodegradation tend to be mirror images. Depth profiles of petroleum related constituent, O_2 , and CO_2 concentrations provide qualitative evidence of the occurrence of aerobic biodegradation in the vadose zone.

- For cases where there is little or no hydrocarbon source at depth, the hydrocarbon vapor profiles will show results at or near the reporting limit (i.e., background or non-detectable concentrations) from the deepest to the shallowest portions of the vadose zone. The concentration of O_2 will be nearly constant throughout the unsaturated zone and CO_2 concentrations will be very low or not detectable.
- Where there is a significant hydrocarbon source at depth and aerobic biodegradation is significant, the hydrocarbon vapor profile will show a decrease in hydrocarbon concentration with increasing distance above the plume that is more rapid than that expected due to diffusion alone. The petroleum hydrocarbon concentration profile will show three distinct zones. The first zone is from the source to a depth where active aerobic biodegradation is not occurring. This zone is representative of anoxic conditions where diffusion is the primary transport mechanism and hydrocarbon vapor concentrations decrease in a linear profile, if at all. The second portion of the profile represents the active zone of aerobic biodegradation (which can be relatively thin compared to the thickness of the unsaturated zone), where there is rapid attenuation of hydrocarbon concentrations coinciding with consumption of O_2 and generation of CO_2 (Johnson et al. 1999). It is not uncommon to see O_2 concentrations decrease from atmospheric levels (20.9%) to 1-2% and CO_2 concentrations increase from less than 1% in the atmosphere to several percent in areas where aerobic degradation is active (DeVaull et al. 1997). In the third zone (above the biologically active layer) hydrocarbon concentrations are typically very low or not detectable and there is generally

elevated O₂ and minimal CO₂. These profiles may vary if there are significant stratigraphic layers of different geologic materials, but this is not the case beneath the former refinery or Hooven.

- For cases where there is a release of hydrocarbons at or near the ground surface (referred to herein as an alternate source) that has migrated into the unsaturated zone, the vertical profiles will be different than the case of a single source at the bottom of the unsaturated zone. If the alternate source is minor, O₂ depletion may only be a few percent below atmospheric levels and vapor concentrations may be reduced to non-detectable or background levels within a few feet of the alternate source. However, where the alternate source is more significant, O₂ concentrations may be fully consumed and aerobic degradation may be limited, in which case, hydrocarbon vapors would be more persistent and migrate by diffusion to shallower and deeper portions of the vadose zone. Consumption of O₂ by an alternate source would also limit the supply of O₂ to deeper portions of the vadose zone, thereby reducing the effectiveness of aerobic biodegradation in deeper portions of the vadose zone where the vapor source is present. If this occurs, vapors from the source at depth diffusing upward and those associated with the alternate source diffusing downward may come together at intermediate depths. Depending on the composition of the alternate source (i.e., petroleum versus non-petroleum) it may be difficult to distinguish whether the vapors are derived from shallow or deep sources. Additionally, the presence of alternate sources and preferential depletion of O₂ at shallow depths in the vadose zone may allow migration of vapors from the source at depth to shallower portions of the vadose zone than would otherwise occur if the alternate source was not present.

Petroleum hydrocarbon constituent and fixed gas (O₂, CO₂, and CH₄) profiles were created for each of the deep nested wells for the historical and most recent monitoring events, as described in the subsections below. The vertical soil vapor profiles were grouped into three general categories, based on the location of the nested vapor monitoring wells:

1. Overlying LNAPL, including nested wells VW-93, VW-96, VW-99, and VW-139 (Figures 3-21 through 3-24)
2. Overlying dissolved phase petroleum hydrocarbons, including nests VW-127 and VW-128 (Figures 3-25 and 3-26)
3. Background areas outside the LNAPL and dissolved phase hydrocarbons, including wells VW-129 and VW-130 (Figures 3-27 and 3-28)

Profiles were constructed for total volatile petroleum hydrocarbons (TVPH) for the monitoring wells located over the smear zone. TVPH is a mixture of hydrocarbon constituents whose composition can vary significantly both spatially (sample interval in each nest) and temporally (across sample events). Generally, TVPH was reported as a single concentration in the soil gas samples collected prior to 2005. For samples collected since 2005, TVPH was estimated by summing the mass of the detected volatile petroleum related hydrocarbon constituents shown in Table 2-8a. For

constituents that were reported as “non-detect”, half the detection limit was used as a surrogate in the estimation of the TVPH concentration. CH₄ was not included in calculation of the TVPH values.

Vertical profiles of benzene and fixed gases were prepared for the nested wells situated over the dissolved phase plume and in background areas located outside the distribution of hydrocarbons attributable to releases from the former refinery. Profiles were not constructed for TVPH for these nested wells due to the low frequency of detection for nearly all of the TVPH constituents. The depth-specific benzene SVSLs are shown on the profiles for reference (note that open symbols representing non-detect results dominate the data from these two wells).

The HSVE system has been operated intermittently each year since 2000, except between December 2007 and October 2009 per amendment of the 2006 AOC by the USEPA. The HSVE system was restarted on October 16, 2009. The sampling events conducted during 2008 and 2009 occurred when the HSVE system was not operating. The HSVE system had not previously remained idle over such an extended period since the system was installed more than a decade ago.

3.3.2.1 NESTED WELLS OVERLYING LNAPL

Vapor profiles for data collected from nested well VW-96 and VW-99 since 1997 support the presence of alternate sources of petroleum hydrocarbons near these two nested vapor monitoring wells, as discussed in Section 2.6.3. The presence of these alternate sources near these wells may be the result of one or more releases of petroleum related chemicals similar to those present in the smear zone. Historical profiles from these two wells generally show a rapid decrease in vapor concentrations from the source to depths between 30 and 45 ft-bgs. A corresponding consumption of O₂ is noted in the fixed gas profiles at these depths, indicating that aerobic degradation is the primary mechanism for these reductions. An increase in vapor concentrations is observed in the TVPH profiles above 30 ft-bgs, during many of the monitoring events, after which concentrations decrease toward the surface. Increasing concentration trends above the 30 foot interval and shallower are not consistent with vapor diffusion from a single vapor source at the water table. Diffusion occurs as a result of a concentration gradient and results in movement of chemicals from areas of high concentration to areas of low concentration. The reverse concentration gradient above 30 ft-bgs is consistent with the presence of an alternate source of petroleum hydrocarbons that may have migrated downward into the vadose zone from a release at or near ground surface.

During monitoring conducted in 2009 within wells VW-96 and VW-99, the TVPH concentrations decrease from the source in the smear zone to shallower depths; however, the reduction in concentrations is less dramatic than observed

during events conducted between 2005 and September 2008. The fixed gas data for these events show that O_2 is being consumed at shallower depths in the vadose zone than observed during previous sample events. The profiles for data collected in 2009 from these two wells show that alternate sources are being aerobically degraded, resulting in a consumption of O_2 in the upper portions of the vadose zone which in turn limits diffusion into deeper portions of the unsaturated zone. This reduces the rate and extent of aerobic biodegradation of the source at depth. The hydrocarbon profiles show a shift from a clear distinction between the source at depth and the alternate sources present in the shallow and intermediate portions of the vadose zone during the previous monitoring events, to a comingling of vapor constituents from the two sources, as observed during the March 2009 and September/October 2009 events.

Per requirement of the USEPA, the HSVE system was not operated in accordance with triggers established in the *OMM Plan* (Trihydro 2007b) between December 2007 and October 2009. Operation of the HSVE system advectively transports O_2 into the deeper portions of the vadose, enhancing the rate of aerobic biodegradation. Therefore, in a case where O_2 is being consumed during aerobic biodegradation of alternate sources, operation of the HSVE system becomes more important in enhancing attenuation of the source at depth. Operating the HSVE system, when O_2 is depleted within the intermediate portions of the vadose zone increases the efficacy of aerobic degradation of the smear zone vapor source.

The vapor profiles for nested well VW-139 situated above the smear zone in the Southwest Quad provides a prototypical examples of aerobic biodegradation of hydrocarbon constituents in the vadose zone. There are no alternate sources of petroleum related constituents observed at this location and therefore, O_2 is able to diffuse into deeper portions of the vadose zone resulting in significant reduction of hydrocarbon concentrations by 30 ft-bgs. It is important to note that the vadose zone is only approximately 40 feet thick beneath the Southwest Quad, compared to 55-60 feet near nested wells VW-96 and VW-99 in Hooven. Even with the thinner vadose zone, concentrations are reduced to non-detect or background levels within 10 feet above the smear zone. If alternate sources were not present near nested vapor wells VW-96 and VW-99, the profiles from these locations would be expected to be similar to those observed at nested well VW-139.

The profiles for data collected in 2009 for nested well VW-93 are consistent with those from a limited hydrocarbon source (i.e., concentrations near background or not detected throughout the profile). These results are similar with previous sampling events conducted since 2005. It is worth noting that historically the concentrations of TVPH measured above the smear zone in this well were similar to those measured in wells VW-96 and VW-99, and much

higher than those observed since 2005. These data support that the vapor source concentrations have decreased dramatically due to the combined effects of aerobic biodegradation and corrective measures system operation.

3.3.2.2 NESTED WELLS OVERLYING DISSOLVED HYDROCARBONS

Nested vapor monitoring wells VW-127 and VW-128 are located over the distribution of dissolved phase hydrocarbons but outside the area of residual LNAPL present in the smear zone. The benzene vapor profiles for these wells are consistent with cases where there is a limited hydrocarbon source at depth. The shallow soil vapor samples show an increase in benzene concentrations relative to deeper samples that is attributed to alternate sources at the ground surface and in the shallow subsurface. Generally, the concentrations observed in the shallow portions of the vadose zone are similar in areas over dissolved phase hydrocarbons and those outside of the distribution of petroleum hydrocarbons associated with releases from the refinery elsewhere in Hooven.

During several of the monitoring events, the vapor profiles from nested well VW-127 show reverse gradients caused by detections in the shallow monitoring intervals. These reverse concentration gradients are considered to be a result of alternate sources of benzene. During these events, O₂ concentrations were generally reduced below atmospheric levels at the intervals with a corresponding increase in benzene concentrations associated with alternate sources. This is attributable to aerobic degradation of the petroleum hydrocarbons associated with these sources within the shallow subsurface. It is anticipated that if the source term above the water table were greater beneath this portion of Hooven, there would be comingling of vapors from this alternate source with vapors diffusing upward from the source as observed in nested wells VW-96 and VW-99 in September/October 2009.

3.3.2.3 NESTED WELLS OUTSIDE OF LNAPL AND DISSOLVED PHASE HYDROCARBONS

Vertical profiles of benzene and fixed gases for nested vapor wells VW-129 and 130 located outside the area of petroleum hydrocarbons associated with the former refinery show that there were not any reported detections of benzene within the deepest monitoring interval during any of the monitoring events conducted at these wells. The vapor profiles for these two wells are consistent with there being no source present at depth.

3.4 SUMMARY OF LINES OF EVIDENCE SUPPORTING NATURAL ATTENUATION

Performance monitoring for any corrective measures program is necessary to demonstrate that the remedy is progressing as anticipated and will meet remedial goals while ensuring that sensitive receptors remain protected.

The USEPA has established additional performance monitoring criteria for remedies incorporating intrinsic natural attenuation processes for degradation of residual impacts (USEPA 1999, USEPA 2003). Performance monitoring programs in these cases must be designed to:

1. Demonstrate that natural attenuation is occurring according to expectations
2. Detect changes in environmental conditions (e.g., hydrogeologic, geochemical, microbiological, or other changes) that may reduce the efficacy of any of the natural attenuation processes
3. Identify any potentially toxic and/or mobile transformation products (although this process is not typical of biodegradation of petroleum hydrocarbons and has not been observed in samples collected at the Chevron Cincinnati Facility)
4. Verify that the LNAPL or dissolved phase plume is not expanding down-gradient
5. Verify no unacceptable impact to down-gradient receptors
6. Detect new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy

These performance monitoring criteria have been achieved during this second semiannual monitoring event based upon the qualitative and quantitative lines of evidence used to demonstrate the stability of petroleum hydrocarbons in the smear zone, protectiveness of sensitive receptors, transformation of petroleum hydrocarbon constituents via intrinsic processes, as well as decreasing petroleum hydrocarbon constituent concentrations and mass over time. During the second 2009 semiannual monitoring event changes in both the dissolved phase and vapor phase conditions at the point of compliance boundaries were identified. These changes have been associated with alternate source of constituents within the vadose zone in portions of Hooven overlying the smear zone, as well as localized release(s) of dissolved phase benzene in the Southwest Quad. An understanding of the affects of these source will be considered during future evaluation and identification of end-points for high-grade and HSVE system operation, as well as part of evaluation of intrinsic natural attenuation mechanisms during implementation of the final corrective measures for groundwater.

4.0 HIGH-GRADE RECOVERY

The high-grade pumping component of the groundwater remedy focuses on seasonal source removal of LNAPL from the lower reaches of the smear zone where the LNAPL saturations remain the greatest. The purpose of high-grade recovery are to (1) further reduce LNAPL mobility at the lowest ambient water table conditions and (2) remove additional LNAPL mass from the smear zone. A summary of the high-grade recovery event conducted during the second half of 2009 is provided in Section 4.1.

Several million gallons of groundwater containing dissolved-phase petroleum hydrocarbons are generated each day during high-grade pumping. This groundwater is treated within the biologically enhanced GAC and transmitted to the constructed wetlands prior to discharge to the Great Miami River under an Ohio EPA administered NPDES Permit. Operation of the GAC system during 2009 is discussed in Section 4.2.

As previously described, the HSVE system remained inactive for 22 months between December 2007 and October 2009, in accordance with the June 30, 2008 modification to the 2006 AOC, which was put in place per USEPA plans for conducting an independent vapor monitoring program in Hooven. The USEPA's vapor monitoring activities were not completed by the end of 2008 as originally intended, so plans for monitoring and system operation during 2009 were further clarified in a February 18, 2009 letter from USEPA to Chevron. The HSVE system remained idle during the time of focused pumping of groundwater and removal of LNAPL (high-grade pumping) beginning in August 2009, when it normally would have been operated in accordance with the 2006 AOC. The HSVE system was restarted on October 16, 2009 following completion of the USEPA investigation. A summary of the HSVE operations during the second half of 2009 is provided in Section 4.3.

4.1 2009 HIGH-GRADE SUMMARY

High-grade recovery began in the Southwestern High-Grade Area on August 19, 2010, once the trigger elevation was reached in monitoring well MW-20S (464.8 feet-above mean sea level [ft-amsl]) as stipulated in Table 4-1 of the *OMM Plan* (Trihydro 2007b). High-grade operations were focused on the use of several production wells in the Southwest Area over the course of the event as follows:

- PROD_20 – August 19 to November 11, 2009
- PROD_20 and PROD_24 – November 11 to November 20
- PROD_19 and PROD_24 – November 20 to November 23

- PROD _19 and PROD_20 – November 23 to November 30
- PROD _19 and PROD_21 – November 30 to December 14

As described in Section 2.1, transducers were deployed within a monitoring network across the high-grade area to collect continuous drawdown data. Groundwater elevation data collected from the transducers are provided in Appendix A. In addition, fluid levels were gauged within an expanded monitoring network at least once each week to evaluate changes in the LNAPL and groundwater elevations in response to high-grade pumping using the various production wells during the 2009 event. The manual fluid level measurements are provided in Appendix B. Groundwater and LNAPL extraction rates from the wells were compared weekly against operational logs at the biologically enhanced GAC and recovery volumes measured in Tank No. 291 and Tank No. 50 throughout the high-grade event. Table 4-1 provides a weekly summary of LNAPL recovery by production well. Table 4-2 provides a summary of the groundwater extraction rates and fluid levels measured within these production wells during the 2009 high-grade event.

4.1.1 FLUID LEVEL AND DISSOLVED PHASE MONITORING RESULTS

As discussed in Section 3.1.1, LNAPL was measured in monitoring wells MW-101S, MW-122, MW-125, and MW-128 during the 2009 high-grade recovery event. These groundwater monitoring wells are located along the western limits of the smear zone in Hooven and LNAPL is not observed within these wells except during high-grade recovery. LNAPL thicknesses were measured from as little as a few hundredths of a foot in monitoring well MW-128 to several tenths of a foot in well MW-125. Groundwater samples were collected from monitoring wells MW-95S, MW-100S, MW-113, MW-124, and MW-129 in November and December 2009 to evaluate dissolved phase concentrations in response to high-grade pumping. These wells are situated at the lateral extent of the dissolved phase plume limits in Hooven and dissolved phase constituents of concern have not been reported in groundwater samples collected from any of these wells since 2004. During monitoring in 2009, there were no reported detections of the volatile constituents of concern above the laboratory reporting limits within samples collected from these five monitoring wells (Table 2-2) and the dissolved phase plume appeared stable during and following high-grade pumping. These observations are consistent with the site conceptual model for plume stability described in Section 1.1.3 with the LNAPL and dissolved phase limits being generally coincident at the lateral edges of the smear zone.

4.1.2 LNAPL RECOVERY

The 2009 high-grade event began by initiating recovery using production well PROD_20, located in the southwestern portion of the smear zone. Production well PROD_20 was selected as the primary production well during this event as the maximum LNAPL thickness prior to pumping was observed within monitoring well MW-140, located over the smear zone in the Southwest Quad. Flow rates were sustained between 2,800 and 3,400 gallons per minute (gpm) from start up through November 11, 2009. High-grade recovery was subsequently shifted to the paired production wells described above, as LNAPL recovery diminished within well PROD_20. The cumulative pumping rate using the paired wells was maintained between 1,970 and 3,050 gpm, until completion of the event on December 14, 2009. The flow rates were adjusted as needed to minimize entrained LNAPL within the extracted groundwater that was being transmitted to the biologically enhanced GAC. High-grade pumping was temporarily discontinued between August 24 and August 25, 2009 for de-scaling of the effluent line from the GAC (Tank 299) to the treatment pond. There were no other interruptions in recovery efforts during the 2009 event.

Figure 4-1 presents a summary of the LNAPL recovery and groundwater extraction rates measured in the production wells during the 2009 event. Approximately 24,000 gallons of LNAPL were recovered using production well PROD_20 between the start of high-grade pumping in August until the end of October. As shown on Figure 4-1 there was an increase in the ambient groundwater levels (measured using monitoring well MW-17, located outside of the influence of the production well) beginning in early-October that corresponded to a significant decrease in the rate of LNAPL recovery. It should be noted that the groundwater extraction rate was increased within well PROD_20 on October 13, 2010 to approximately 3,400 gpm; however, the daily LNAPL recovery rate continued to decrease as a result of the increasing ambient water table.

Approximately 1,500 gallons of LNAPL were recovered from early November until the completion of the event on December 14, 2009. The following is a summary of LNAPL recovery within the paired wells over this timeframe:

- PROD_20 and PROD_24: 100 gallons of LNAPL
- PROD_19 and PROD_24: 130 gallons of LNAPL
- PROD_19 and PROD_20: 640 gallons of LNAPL
- PROD_19 and PROD_21: 630 gallons of LNAPL

The high-grade recovery event was discontinued on December 14, 2009 due to a significant decrease in the LNAPL recovery rate over the previous week, with only 24 gallons of LNAPL recovered between December 7 and December 14, 2009; combined with an increasing ambient water table.

Figures 4-2 and 4-3 present the drawdown and LNAPL thickness maps for the fluid levels measured on September 11, 17, and 18, 2009. Fluid level data could not be collected in Hooven during the September 11 gauging event due to the USEPA vapor monitoring activities. Instead, fluid levels from gauging performed in Hooven between September 17 and 18 were used to generate Figures 4-2 and 4-3. The drawdown for each well was calculated as the difference in groundwater elevation measured in mid-September and the ambient groundwater elevations reported prior to high-grade pumping on August 19, 2009. The drawdown for each well reported on Figure 4-2 was corrected for the ambient changes in the water table as measured in monitoring well MW-17, located outside the influence of high-grade pumping in the Southwest Area. Drawdown was greatest within production well PROD_20 (3.99 feet) and extending to the northwest. LNAPL accumulations as shown on Figure 4-3 were thickest within the monitoring wells MW-96S (0.65 feet) and MW-99S (2.18 feet) located in the central portions of Hooven. The elevated thicknesses measured in these two wells are indicative of higher LNAPL saturations within the lower portions of the smear zone at these locations.

A total of 25,499 gallons of LNAPL were recovered during the 2009 high-grade event. Table 4-3 provides a summary of cumulative and daily LNAPL recovery rates, average groundwater extraction rates, as well as the LNAPL removal efficiency in each of the production wells during 2009. LNAPL was recovered at a maximum rate of 233 gallons per day from production well PROD_20. Approximately 4,108,000 gallons of groundwater were also recovered each day using this production well, with a LNAPL recovery efficiency of 17,600 gallons of groundwater removed for each gallon of LNAPL recovered. The LNAPL recovery efficiency was nearly 5 times greater using well PROD_20 compared to pumping from the paired wells during this event. This data supports findings from the 2007 event, that pumping from a single production well at a higher rate (up to 3,400 gpm as performed during this event) results in increased LNAPL recovery, which will result in further reduction in the LNAPL saturations in the lower reaches of the smear zone.

High-grade triggers may not have been reached in the Southwest Area during 2009 in the absence of hydraulic containment pumping that was being performed using wells PROD_15 and PROD_24. Hydraulic containment was being performed in response to detections of dissolved phase benzene in POC well MW-133 in April 2009. For comparison, high-grade triggers were achieved under non-stressed conditions in June 2007 and high-grade recovery

was performed from June 7 until December 14 that year. During the 2007 high-grade event approximately 21,000 gallons of groundwater were removed for each gallon of LNAPL recovered. The LNAPL recovery efficiency during this event was nearly twice that compared to 2009 with approximately 40,000 gallons of groundwater removed for each gallon of recovered LNAPL (when averaging the LNAPL removal efficiency for all of the production wells listed on Table 4-3). It is expected that additional LNAPL recovery and further reductions in LNAPL saturations will be realized following completion of future high-grade events performed when triggers are reached under ambient water table conditions.

4.1.3 REVISED TRIGGER ELEVATIONS

LNAPL recovery is undertaken during low water table conditions, based on historical trends and field observations during seasonal dry periods. LNAPL appears in wells and is recoverable as a function of water table elevations (triggers) as they relate to the smear zone. The water table must be low enough to expose the approximate bottom third of the smear zone before LNAPL can be recovered. The goal of high-grade pumping is to use focused groundwater extraction to maximally expose the smear zone and recover LNAPL during low water table conditions. Maximal exposure of the smear zone occurs when the water table is drawn down below the previous minimum groundwater elevation. Thus, the minimum historical groundwater elevation within a well is used to establish targets for initiating high-grade recovery. With each successful high-grade event, the depth of maximum smear zone exposure will be lowered, thereby establishing new, lower triggers for starting high-grade recovery over subsequent events. The trigger for initiating high-grade recovery is determined via the following equation:

$$\text{Pumping Trigger} = PT_i + s_{i,j}$$

Where:

PT_i = Pumping target at monitoring well location i ; value is the historical minimum water table elevation in ft-amsl

$s_{i,j}$ = Expected drawdown at monitoring well location i caused by high-grade pumping at production well j

As noted by the subscripts in the above equation, pumping triggers are specific to the monitoring location and the production well. Prior to each high-grade event, new pumping triggers will be calculated by analyzing the fluid level data from the preceding event. New triggers will be established at locations where the water table was lowered to a new minimum elevation. Otherwise, triggers from the preceding year will be carried forward. The expected drawdown will be based on fluid level monitoring data collected during previous high-grade pumping events.

As summarized on Table 4-4, trigger elevations for initiating high-grade pumping using production wells PROD_20 were re-calculated for monitoring wells MW-20S, MW-93S, MW-96S, and MW-99S situated within the Southwest Area based on the minimum groundwater elevation reported in each of these wells since 1990, as well as the drawdown data collected during high-grade pumping since 2005. The lowest groundwater elevation observed in monitoring wells MW-20S, MW-93S, and MW-96S occurred on October 16, 2009 during high-grade recovery performed using production well PROD_20. Whereas, the lowest elevation observed in well MW-99S occurred on October 1, 2007 during high-grade recovery using production well PROD_19. Using the maximum drawdown reported during any of the high-grade events, the groundwater elevation triggers for initiating high-grade recovery are between 1.4 (MW-20S) and 2.9 (MW-96S) feet lower than those established within the *RIP* (Trihydro 2007a) and *OMM Plan* (Trihydro 2007b).

It should be noted that in evaluating historical fluid level data collected from monitoring well MW-20S, these revised high-grade trigger levels would have been achieved in 10 of the 12 years (1992 to 2004) prior to 2005 when high-grade recovery activities began at the Chevron Cincinnati Facility. This corresponds to a frequency of 85% for annual high-grade occurrence listed on Table 4-4. The frequency of high-grade occurrence within wells MW-93S, MW-96S, and MW-99S would be 88%, 25%, and 25% respectively, based on fluid level data collected between 1997 and 2004. The frequency of high-grade occurrence estimated for wells MW-96 and MW-99 is likely biased low as a result of infrequent fluid level measurements from these wells between 1997 and 2004 (6 measurements per year). The next high-grade event will be conducted using these revised triggers. During the next event, LNAPL emergence within the trigger monitoring wells and LNAPL recovery within the production well will be evaluated to confirm the appropriateness of these revised high-grade triggers for initiating future events.

4.2 BIOLOGICAL ENHANCED GAC SYSTEM OPERATION

The biologically enhanced GAC is designed to remove dissolved phase petroleum hydrocarbons, primarily BTEX from extracted groundwater. Extracted groundwater is transmitted to the GAC for treatment from one or more of the production wells located at the Facility. The GAC treatment process is discussed in further detail in the OMM Plan (Trihydro 2007b).

Following treatment in the GAC, groundwater is transmitted to the sedimentation pond and constructed wetlands prior to discharge to the Great Miami River through the wetlands outfall. Groundwater samples are collected weekly at the wetlands outfall to evaluate compliance with NPDES discharge limits. A composite groundwater sample was collected each week using an automated sampler, which collects a sample aliquot every 45 minutes over a 24-hour period.

Composite samples were analyzed by TestAmerica Laboratories located in North Canton, Ohio to evaluate compliance with discharge requirements set forth in the Facility's NPDES permit. Groundwater samples are analyzed for flow rate, pH, biological oxygen demand, total suspended solids, oil and grease, total lead, as well as dissolved phase concentrations of BTEX, total phenols, and 1,2-dichloropropane. Monthly and daily concentration and loading limits are established for these constituents. None of the effluent limits were exceeded in the weekly samples collected from the outfall during the reporting period during the high-grade recovery or hydraulic containment pumping conducted during the second half of 2009.

4.3 HSVE SYSTEM OPERATION

Chevron installed the HSVE system as an interim measure for reducing petroleum hydrocarbon mass beneath Hooven (ERM 1999). Pilot testing to determine the effectiveness of soil vapor extraction technology was conducted in June and November 1998. Based upon the results of the pilot testing and completion of a remedial options analysis in June 1999, it was determined that HSVE presented the best available technology for removing volatile hydrocarbons, while minimizing disruptions to residents in Hooven.

The HSVE system is comprised of three six-inch diameter, Schedule 40 carbon steel pipes that extend from the western edge of the facility beneath State Route 128 continuing under Hooven, coincident with the distribution of refinery related hydrocarbons (Figure 4-4). Line No. 1 extends westward beneath Hooven Avenue, Line No. 2 is located beneath Brotherhood Avenue curving to the south towards Hooven Elementary School, and Line No. 3 is located beneath Ohio Street. The well screens for each of the lines were installed approximately five feet above the 15 year maximum groundwater elevation at the time of installation (478 feet above mean sea level (ft-amsl) for Line Nos. 1 and 2 and 475 ft-amsl for Line No. 3).

Pilot test, modeling, tracer test, and performance monitoring results indicate a radius of influence of the HSVE system between 125 and more than 450 feet from the extraction lines (Chevron 2010b). A conservatively low radius of influence of 200 feet around each of the horizontal vapor extraction lines is presented on Figure 4-4. No structure in Hooven, situated over the distribution of petroleum hydrocarbons associated with releases from the former refinery, is more than 200 feet from one of the HSVE extraction lines, with the exception of a single residence located approximately 250 feet north of Line No. 3. Therefore, operation of the HSVE system affects soil vapor conditions within the deeper portions of the vadose zone throughout portions of Hooven overlying the smear zone.

The system commenced operation in November 1999 following installation of HSVE Line No. 1. Lines No. 2 and No. 3 were installed in 2000 and brought online during the first quarter 2001. Currently, operation of the HSVE occurs during seasonal low water table conditions, when lower portions of the smear zone (which contain the highest mole fraction of volatile hydrocarbons) are exposed in the vadose zone. As stipulated in Paragraph 11.c of the 2006 AOC, the HSVE system shall be operated during periods of high-grade recovery when focused pumping conditions allow for exposure of the lower portions of the vadose zone, or when the low water table conditions allow further recovery of volatile hydrocarbons. The trigger elevation for operation of the HSVE system was established at a groundwater elevation of 465.9 ft-amsl measured in well MW-96, as defined in the *OMM Plan* (Trihydro 2007b).

4.3.1 2009 OPERATIONS SUMMARY

The HSVE system remained inactive for nearly 22 months from December 2007 until October 2009, as stipulated by the USEPA within the Order Amendment dated June 30, 2008 and clarified in correspondence dated February 18, 2009. As such, the HSVE system was not restarted until October 16, 2009 following completion of the USEPA vapor monitoring activities in Hooven. The system was then operated continuously until completion of the high-grade recovery event on December 18, 2009. As summarized on Table 4-5, during 2009 the HSVE system was operated by cycling each extraction line with Line No.1 being operated for 23 days, Line No. 2 for 43 days, and Line No. 3 for 28 days. Approximately 34,000 pounds of organic carbon was recovered via operation of the HSVE system in 2009. The estimated organic carbon removed from the system is calculated based upon the concentration of total petroleum hydrocarbons and CH₄ reported in the influent vapor samples, average flow rate recorded at the wellhead, and hours of operation over the reporting period.

Operational data is collected at each of the process lines during operation of the HSVE system including the rate of airflow and vacuum, as well as the fixed gas concentrations including O₂, CO₂, CH₄, total organic vapors, and the lower explosive limit. Table 4-6 presents a summary of the operational monitoring data recorded at each of the extraction lines. In general, during operation of each extraction line, O₂ concentrations would increase over time within the influent, with a corresponding decrease in CO₂, CH₄, total organic vapors, and the lower explosive limit.

Combined influent and effluent vapor samples were collected monthly to demonstrate compliance with the Hamilton County Permit to Operate. The compliance monitoring data is compared to permitted operational limits on a quarterly and semiannual basis. Table 4-7 presents a summary of compliance monitoring data collected from the system during operation in 2009, as well as a summary of the calculated organic carbon extraction and emission rates (reported in pounds per hour, pounds per day, and tons per year). Monthly emission rates were below the allowable limits of 6.25

pounds per hour. The average emission rate was approximately 0.7 pounds per hour during operation of the system in 2009.

Figure 4-5 presents the estimated organic carbon removed beneath Hooven via operation of the HSVE system since November 1999, as well as the benzene and total petroleum hydrocarbon concentrations in the influent. More than 530,000 pounds of petroleum hydrocarbons have been removed from the vadose zone beneath Hooven and the Southwest Quad since 1999. The HSVE system was designed to remove volatile petroleum hydrocarbons at a high rate initially, with an expectation that the mass removal rate would gradually diminish as the volatile petroleum hydrocarbons within the smear zone were depleted, at which time the system would be operated intermittently and ultimately shut down. It's anticipated that when the system is ready to be permanently shut down, the remaining hydrocarbon mass within the influence of the system would diminish to a level where continued operation does not result in reduction of soil vapor concentrations beyond those observed via aerobic biodegradation alone, as can be observed in the vapor source concentration trends for nested soil vapor monitoring well VW-93 (Figure 3-15). However, in some portions of Hooven, volatile petroleum hydrocarbon concentrations have persisted in the smear zone, despite operation of the HSVE system. This may be explained by alternate sources of petroleum hydrocarbons identified in the vadose zone near these locations, as discussed previously herein. Aerobic biodegradation of these alternate petroleum hydrocarbon sources in the shallower portions of the subsurface preferentially utilizes O₂. As such, O₂ transport to deeper depths where hydrocarbons from the former refinery are present at the water table is limited; therefore decreasing natural attenuation within the smear zone. This can be observed in the vapor source trends for wells VW-96 and VW-99 (Figures 3-16 and 3-17). In portions of Hooven where alternate sources of hydrocarbons are present at shallower depths, the HSVE system not only removes volatile petroleum hydrocarbons, but also advectively transports O₂ to the deepest portions of the vadose zone where it would otherwise not be present. Aerobic biodegradation, and not source removal, may be the primary mechanism degrading the volatile petroleum hydrocarbons present in the smear zone, hence the difference in vapor source concentrations observed in vapor well VW-93 compared to wells VW-96 and VW-99 since 1999.

5.0 GULF PARK

A former products transfer pipeline corridor, consisting of five 6-inch diameter lines that connected the former refinery with a loading terminal on the Ohio River, was located beneath the Gulf Park property. The pipelines carried three grades of gasoline, kerosene, aviation fuel, diesel, and fuel oil during use between 1930 and the mid-1980s.

Hydrocarbon-stained soil was discovered in Gulf Park in January 1993 at approximately 10 to 14 feet below grade. Several subsurface investigations to define soil and groundwater conditions and the extent of petroleum hydrocarbons were conducted between 1993 and 1994.

Based upon the findings of these investigations, a bioventing system was installed in the area that is now the westernmost soccer field at Gulf Park in 1996. It consists of 14 air injection wells designed to deliver approximately 30 to 35 standard cubic feet per minute (scfm) to each injection well, and a blower. Valve controls for the air injection wells installed in the soccer field area are located in a nearby Valve Control Shed (VCS No. 1). A bioventing system expansion was installed between August and October 2000, consisting of an additional 38 bioventing wells constructed of 2-inch diameter PVC casing and 0.010-inch slotted screen. These bioventing wells were completed below grade and connected to a separate Valve Control Shed (VCS No. 2). Figure 5-1 shows the layout of the two bioventing systems installed at Gulf Park.

There are two primary lines of evidence used to evaluate the remedy performance at Gulf Park. First, soil vapor data is collected from selected nested wells installed in the shallow and deep portions of the vadose zone to evaluate fixed gas concentrations during times when the bioventing system is active and inactive. A discussion of the biovent operations and soil vapor monitoring data collected during the second half of 2009 are provided in Section 5.1.

Second, dissolved phase monitoring is conducted annually in Gulf Park to evaluate temporal and spatial trends in the dissolved phase constituents of concern, as well as natural attenuation indicators. Groundwater samples were not collected during the second half of 2009, in accordance with the schedule outlined within the *OMM Plan* (Trihydro 2007b). Therefore, an evaluation of dissolved phase hydrocarbon trends is not provided herein.

In order to isolate petroleum hydrocarbons present in the smear zone along the east bank of the Great Miami River in Gulf Park a partially penetrating sheet pile barrier and river bank stabilization measures were performed along the northern portion of the smear zone that abuts the river bank. The sheet pile barrier placement was selected based on smear zone morphology with the objective of eliminating potential petroleum hydrocarbon flux towards the river.

Section 5.2 presents a summary of the sheet pile installation and river bank stabilization measures performed along the northern transect during the second half of 2009. A second section of the sheet pile wall and bank stabilization measures were proposed along the southern transect in the Park. Installation and stabilization measures were not completed in 2009 along the southern transect due to refusal of a third-party property owner to allow access to this portion of the river bank. Additional assessment activities are slated to be performed during the second half of 2010 to evaluate options along the southern limits of the smear zone that are in contact with the river bank.

5.1 BIOVENT SYSTEM PERFORMANCE MONITORING

Bioventing stimulates intrinsic biodegradation of petroleum hydrocarbons in the vadose zone by injecting air at low flow rates to provide sufficient O₂ to sustain aerobic microbial activity. Airflow is injected at rates designed to maximize O₂ delivery to the subsurface while minimizing volatilization of hydrocarbon constituents, thus eliminating the necessity for vapor intrusion or ambient air pollution control measures.

Startup and shutdown criteria for the biovent system are related to groundwater trigger levels beneath Gulf Park. Historic soil vapor monitoring data indicate that higher respiration rates occur within the lower portions of the smear zone. However, this portion of the smear zone is only exposed during low water table conditions. The groundwater level is typically above the trigger level elevation from January through June and below the trigger level intermittently from June through December. The period of low water table conditions is considered the seasonal bioventing operation period. Figure 5-2 presents the hydrographs from the trigger monitoring wells for 2006 through 2009. As shown, groundwater elevations were generally below the trigger levels within wells GPW-5S and TH-2 from June until the end of November 2009. Thereafter, the water levels rebounded and then fluctuated above and below the trigger elevation for the remainder of 2009.

The bioventing system at Gulf Park was operated continuously during the second half of 2009 after startup on July 7, 2009 through March 2, 2010, with only minor shut downs due to power outages. Each bioventing well has a valve to regulate air flow and a port used for monitoring temperature, pressure, and air flow. The system monitoring activities performed during operation of the biovent system in the second half of 2009 consisted of:

- Recording operational parameters (pressure, flow rate, and temperature) periodically at the process blower in order to document the blower performance
- Measuring air flow parameters in each of the biovent wells weekly in order to document the amount of air delivered to the subsurface through each injection well

- Gauging fluid levels within the system trigger wells (GPW-5S and TH-2) on a weekly basis to determine the schedule for system startup and shutdown
- Collecting field measurements of soil vapor composition including total organic vapor, pressure, and fixed gas concentrations (O_2 , CO_2 , and CH_4) to qualitatively evaluate system effectiveness

5.1.1 BIOVENT SYSTEM PERFORMANCE RESULTS

During system inspections and each time air flow adjustments were made, performance parameters for active (i.e., valve not closed) injection wells were monitored within VCS No. 1 (Lines BV-1 through BV-14) and VCS No. 2 (BVW-1 through BVW-38). Biovent wells in VCS No. 1 contain analog, vane-style flow meters, which allow for measuring instantaneous flow rates. Biovent lines located in VCS No. 2 were installed with sensor ports to allow for measurement of pressure, temperature, and differential pressure in order to calculate standard air flow rate.

Pressure in the individual biovent wells in VCS No. 2 was measured using a digital manometer. Injection air temperature measurements for the biovent expansion system were collected from dedicated dial gauge thermometers installed on each vent line. Flow rates measured at individual biovent well lines were measured using a Dwyer flow sensor manufactured to measure differential pressure in a 2-inch diameter pipe. The flow sensor was connected to a digital manometer, and differential pressure values provided by the manometer were recorded. The recorded values were later converted to volumetric flow rates and corrected to standard conditions.

During the second half of 2009, biovent system control valves were periodically adjusted to deliver a target 35 scfm of air to each biovent well. Based upon average flow rates measured at the biovent wells and recorded operation times, approximately 472,860,000 standard cubic feet of process air was injected into the expanded biovent system area during the periods of operation that occurred in the second half of 2009 between July 7, 2009 and December 31, 2009. The biovent well performance measurements, including dates and time of operation, are presented in Appendix I.

5.1.2 SOIL VAPOR MONITORING RESULTS

Soil vapor conditions including fixed gases, total organic vapor, and pressure were measured within selected nested vapor monitoring points including VP1-25S, VP1-25D, VP1-50S, VP2-25S, VP2-50S, VP3-35S, VP3-35D, VP4-25S, VP4-25D, and VP6-35S, based on access to the vapor points and water table elevation. Due to the groundwater elevation at the time of measurement, several of the deeper vapor monitoring points could not be monitored. Soil vapor field measurements were collected prior to system start-up on July 7, 2009, a day before shutdown on March 2, 2010

and four additional events after shutdown to track the rate in which the subsurface vapors return to equilibrium. Results of field measurements collected from accessible vapor monitoring points during July 2009 and March 2010 are included in Appendix J.

Table 5-1 presents the results of fixed gas and total organic vapor measurements collected from soil vapor monitoring points during July 2009 and March 2010. Comparison of the fixed gas concentrations measured prior to system start-up and when the system was active indicates that bioventing has a measurable impact on the vadose zone beneath the Park. There was an increase in O₂ concentrations approaching atmospheric levels following startup of the system, with a corresponding decrease in CO₂, CH₄, and total organic vapors. O₂ concentrations within vapor points VP1-25, VP1-50, VP3-35, and VP4-25S were elevated prior to the start up of the system indicating that petroleum hydrocarbons have been degraded in the smear zone via historical operation of the biovent system beneath this portion of the Park.

These field screening results may be used in the future to support termination of bioventing beneath portions of the system where aerobic conditions prevail throughout the year and petroleum hydrocarbons have been depleted. Additional air delivery can then be supplied to those portions of the Park where petroleum hydrocarbons persist and anaerobic conditions are observed during periods when the system is inactive. Additional monitoring activities within the Park are planned for the second half of 2010 to further assess soil quality within the smear zone and determine if any modifications to the design or operation of the biovent system are warranted.

5.2 BANK STABILIZATION AND BARRIER CONSTRUCTION

On February 28, 2007, Chevron submitted an evaluation of containment options for petroleum hydrocarbons present near the east bank of the Great Miami River within the *Evaluation of Engineered Options along the East Bank of the Great Miami River, Gulf Park, Cleves, Ohio* (Trihydro 2007c) in fulfillment of Section VI.11.g of the 2006 AOC. The USEPA provided comments regarding the options analysis on January 24, 2008. The options analysis was subsequently revised and finalized incorporating the USEPA comments. The selected option included stabilization of the river bank combined with installation of a partially penetrating sheet pile wall to prevent erosion of bank soils in contact with the smear zone. Upon approval of the preferred option by the USEPA, Chevron proceeded to prepare detailed designs for the remedy, and submitted them in a document titled *Remedial Measures Work Plan for Sheet Pile Barrier Construction and Bank Stabilization along the East Bank of the Great Miami River, Gulf Park, Cleves, Ohio* (Trihydro 2008). Based on comments to the design, Chevron subsequently revised the plans and submitted the final approved design in an updated report dated September 17, 2008.

The bank stabilization and barrier construction activities were completed between September and October 2009 in general accordance with this work plan. An as-built barrier alignment is shown on Figure 5-1. Note that the basemap contours shown on Figure 5-1 are from the Hamilton County GIS Database dated July 2004. Since this time, the east bank of the Great Miami River has been eroded to varying degrees inland along the Park. The portion of the sheet pile barrier alignment parallel to the river approximates the 460 ft-amsl contour as surveyed prior to installation of the barrier in 2009, as this was the lateral alignment design criteria provided in the work plan. While the riverbank has shifted eastward between two to six feet in this area, the alignment shown represents the actual barrier location relative to other stationary site features (e.g., structures, roads, and wells). Basemap contours will be updated on future Gulf Park figures upon availability of such data from Hamilton County. Additional details regarding construction activities are provided below and organized by project component in the general order performed.

5.2.1 SITE PREPARATION

On September 29, 2009 construction activities commenced with the installation of perimeter fencing and warning signs. In order to minimize any disturbance to Indiana Bat roosts that were potentially present within the Park, clearing and grubbing activities were not started until October 1, 2009. An approximate 0.1-acre area, extending 15 to 20-feet from the river's edge, was cleared to facilitate grading of the low-sloping bench. Following clearing and grubbing activities, overburden was stripped and stockpiled for subsequent placement on the re-contoured low-sloping bench. Silt fence and hay bale lined ditch dykes were installed as erosion control.

5.2.2 SHEET PILE BARRIER WALL

Prior to installation of the sheet piles, a work platform was constructed along the length of the barrier to accommodate pile driving activities. Throughout sheet pile installation, the work platform remained above the water line and allowed access for necessary equipment.

Pile driving activities began on October 7 and were completed by October 14, 2009. The partially penetrating steel sheet pile barrier wall was installed with piles driven from north to south. The wall was constructed with 30-foot-long PZC-12 steel sheet piles. The piles were driven into the ground surface using a track-mounted sheet pile driver to a top-of-pile target elevation of approximately 466 ft-amsl from the northern limits of the barrier sloping down to 465 ft-amsl at the southern tie in of the wall. The sheet piles were delivered in seal-welded pairs with a water-swelling sealant applied to the non-welded joint interlocks.

A professionally licensed surveyor established control points throughout the project area and completed an as-built survey of the constructed sheet pile barrier wall. Each of the sheet piles were emplaced within four inches of the target depth, with the vast majority driven within two inches of the design elevation. Piling was driven without refusal.

5.2.3 LOW-SLOPING BENCH

Grading activities began following installation of the partially penetrating sheet pile wall to create a low-sloping bench along the east bank of the Great Miami River. The existing bank and work platform was brought to the proposed low-sloping bench grade using native soils excavated during sheet pile barrier wall installation. The soils were placed in 8-inch lifts, and compacted with at least six passes of a smooth drum vibratory roller.

5.2.4 RIP RAP REVETMENT SYSTEM

A rip-rap revetment system was constructed along the outboard portion of the sheet pile barrier to protect the partially penetrating wall from scour during future flood events. Following installation of the sheet pile wall, Ohio Department of Transportation Class C rip-rap was placed on the river side of the barrier wall. A 3-foot key trench was excavated and approximately 6-feet of rip-rap was placed to the angle of repose outboard of the barrier wall.

5.2.5 LOW-SLOPING BENCH STABILIZATION

During bench construction, GeoWeb™ was installed from the top of slope to the extent of the low-sloping bench. GeoWeb™ is a 6-inch thick polyethylene cellular confinement mat system that confines and reinforces the upper soil layer. Approximately, 4 to 6-inches of final grade material was placed above the soil filled GeoWeb™ mat. Due to the lack of growing season following the completion of the barrier wall construction, a turf reinforcement mat (Enkamat® TRM) was installed across the face of the slope and the low-sloping bench. The reinforcement matting was not specified in the work plan, but was added to further enhance bank stability. Subsequently, a broadcast spreader was used to apply seed and straw to the area, after which a fertilizer-containing tactifier was sprayed over the area. The seeding activities were completed on October 27, 2009.

6.0 REFERENCES

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